THE MICROWAVE HEATING OF OIL SHALE

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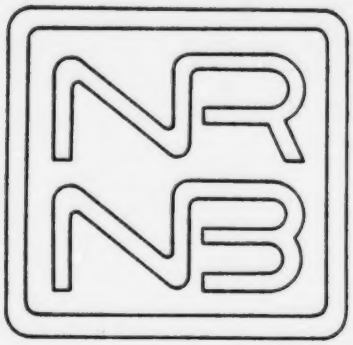

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THE MICROWAVE HEATING OF OIL SHALE

by

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1. ABSTRACT

Microwave heating is one of many processes now being investigated as a possible technique for recovering oil from oil containing shale.

In this exercise several shale samples from the Albert County deposit were heated using a Cryodry Model 1-2LP Power Applicator-Generator. The incident power level was maintained at 100w with a helium flourate of 600 ml/min. The gases released were analyzed with the following results: carbon dioxide, methane, carbon monoxide and ethylene were present in all samples. Small amounts of acethylene and ethane were identified in some of the samples tested. Total gas volumes ranged from a low of 47.82 cm^3 for sample A2-07 to a high of 514.4 cm^3 for sample A10-03.

The oil yield from the samples averaged 88.8% of that reported by the Fischer Assay technique. Gas yields were significantly higher for the microwave process ranging from a low of 1.12 times to a high of 11.3 times that produced by the Fischer Assay method.

The results of tests performed to determine the percentages by weight of bitumen extracted as a function of reaction time were in accordance with those presented in (2).

2. INTRODUCTION

The rapidly dwindling supplies of conventional crude oil and natural gas deposits have caused a major stir in the energy circles of both Canada and the United States. The predicted petroleum shortage for the coming decades has resulted in massive programs for the development of "synthetic" substitutes for these products. In Canada, the emphasis, at the moment, is on the recovery of oil from the rich tar sands of Alberta. In the United States the tapping of vast quantities of oil trapped in the shale deposits of Colorado, Utah and Wyoming could very well be the answer to their future energy problems. There are an estimated 2.1 quadrillion barrels of oil contained in the shale deposits of the world. If suitable method could be derived to recover these reserves, dependence on conventional sources would be eliminated.

Research into the development of a commercially viable shale oil recovery process in the United States has been going on since the early 1960's. Studies have been made into the feasibility of both in-situ and surface retorting operations and various methods have been put forth. Surface retorting processes can be classified into one of five categories:

Class I - Indirect heating by radiation and conduction through retort walls.

Class II - Direct heating by circulation through shale of hot gases resulting from combustion of a portion of the carbonaceous material in the

Class III - Direct heating by circulation through shale of an externally heated carrier fluid.

Class IV - Heat transfer by contact between shale and hot recycled solids.

Class V - Other heat transfer methods, including microwave, laser and circulation of a substance that releases heat by chemical or nuclear reaction.

The problems with surface techniques, irregardless of the method, are that they produce enormous quantities of refuse, spent shale, that must be disposed of and the mining of the shale rock is a very expensive operation.

The development of in-situ retorting processes will eliminate these problems. In-situ techniques are divided into two categories. The first includes processes which employ only the natural permeability of the shale deposits. The second includes all the processes which create artificial permeability. Most shale deposits are impermeable and therefore it is essential that an inexpensive method of creating permeability be established.

The newest trend of recovery processes falls into the category of the surface retorting techniques. While only in the development stages, the use of microwaves in the recovery of oil from shale deposits has some distinct advantages over conventional surface methods. Some of these include:

I. - possible development of an in-situ process.

II. - eliminating intermediate processing operations.

III. - disposal of waste material does not create an environmental problem.

Tests have also been carried out on the use of microwaves to extract oil from the tar sands (2). Results show the microwave produced tar sand crude to be of a much higher quality than the convertional tar sand crudes. This enables one to eliminate the initial stage of refining that the tar sand crudes must be subjected to. Further studies (2) indicate that 16% more oil can be extracted by the microwave technique.

This report investigates the use of microwave power in recovering oil trapped in the shale deposits of Albert County, New Brunswick. A prototype reactor model was designed and constructed so as to enable heating of a small sample of the oil containing shale. The reactor circuit was equipped with a sampling valve and a Gas Chromatograph to make possible the analyzing of the gaseous components released during the cooking process.

3. APPARATUS

The apparatus employed in the performance of this study consisted of the reactor circuit as depicted in Figure (1). The reactor tube was made of quartz with a diameter of approximately 20 mm. The length was not important and varied from test to test. The microwave power was supplied by a Cryodry Model 1-2LP Power Applicator-Generator capable of a variable power output of 0 - 3.0 kw at a frequency of 2450 ± 50 MH

The Gas Chromatograph used to analyze the released gases was a Gow Mac Series 550 Thermal Conductivity Detector employing a 1'5" x ¼" copper column containing a spirocarb packing. The output from the chromatograph was recorded on a Speedomax W 1mv chart recorder.

The Helium flowrates through the Gas Chromatograph and the reactor tube were measured by Matheson Gas Products rotameters using 601 and 603 tube sizes, respectively.

A Mettler H45 balance was used to weigh the samples before and after heating. Two stop watches were used, one to time the reaction and the other the injection time for the samples. A 25 ml soap bubble meter was used to ensure that the 601 rotameter was reading an accurate flow for the helium through the chromatograph.

Gas cylinders of carbon monoxide, carbon dioxide, methane, ethane, ethylene and acethylene along with regulators for these cylinders were needed for calibration of the Gas Chromatograph.

Other equipment included 1/8" stainless steel tubing, stainless steel sampling loops 1cc, 2cc and 5cc in volume and a sampling valve.

4. PROCEDURE

The initial stages of the project involved the design and construction of a suitable reactor circuit. The final system was based on that used by Bosisio et al [2]. The circuit and microwave equipment were set up in Room 210 of Head Hall, University of New Brunswick.

4-(a) The Gas Chromatograph

Before actual testing took place, the Gas Chromatograph was calibrated using the various gases that were expected to be found in the shale samples. The chromatograph parameters were adjusted to obtain a carrier gas flow rate (helium) of 60 ml/min., a bridge current of 100 mA and temperatures for the detector, column and injection part of 155, 165 and 200°C respectively. The retention times for the gases were then determined by sending a sample of each gas diluted with helium into the chromatograph, Figure (2). The samples had to be diluted as pure gas samples tended to have shorter retention times.

The chromatograph was calibrated for amount by putting pure samples of 1 and 2 cc through the column. With these results a plot of peak height versus volume of gas was constructed.

4-(b) Test Procedure I

A small rectangular sample of the shale rock approximately 23 mm x 10 mm x 10 mm in size was first weighed and placed

inside the quartz reactor tube. The tube was inserted into the waveguide cavity. One end of the quartz vessel was then connected to a supply of helium by 1/4" polyethylene tubing. The flowrate was adjusted by a Matheson 603 rotameter. The purpose of the helium was to carry the released gases to the Gas Chromatograph for analysis. The other end of the reactor was connected to a pyrex cold trap needed to condense any high molecular weigh hydrocarbons in the system. Once this connection was made, the valve, shown in Figure I, was opened slightly so as to relieve any pressure that might build up in going from the larger volume cold trap to the 1/8" stainless steel line that carried the samples to the Gas Chromatograph.

The rotameter in the polyethylene line to the reactor was adjusted to obtain a helium flowrate of 600 ml/min. The helium was allowed to flush the system, removing any trapped air. To test for air or other gases in the line, samples were sent through the 2 cc sample loop into the Gas Chromatograph. The parameters for the Chromatograph were maintained at exactly the same values as during the calibration procedure. The removal of all air was signalled by the failure of any peaks to register on the chart recorder connected to the Gas Chromatograph.

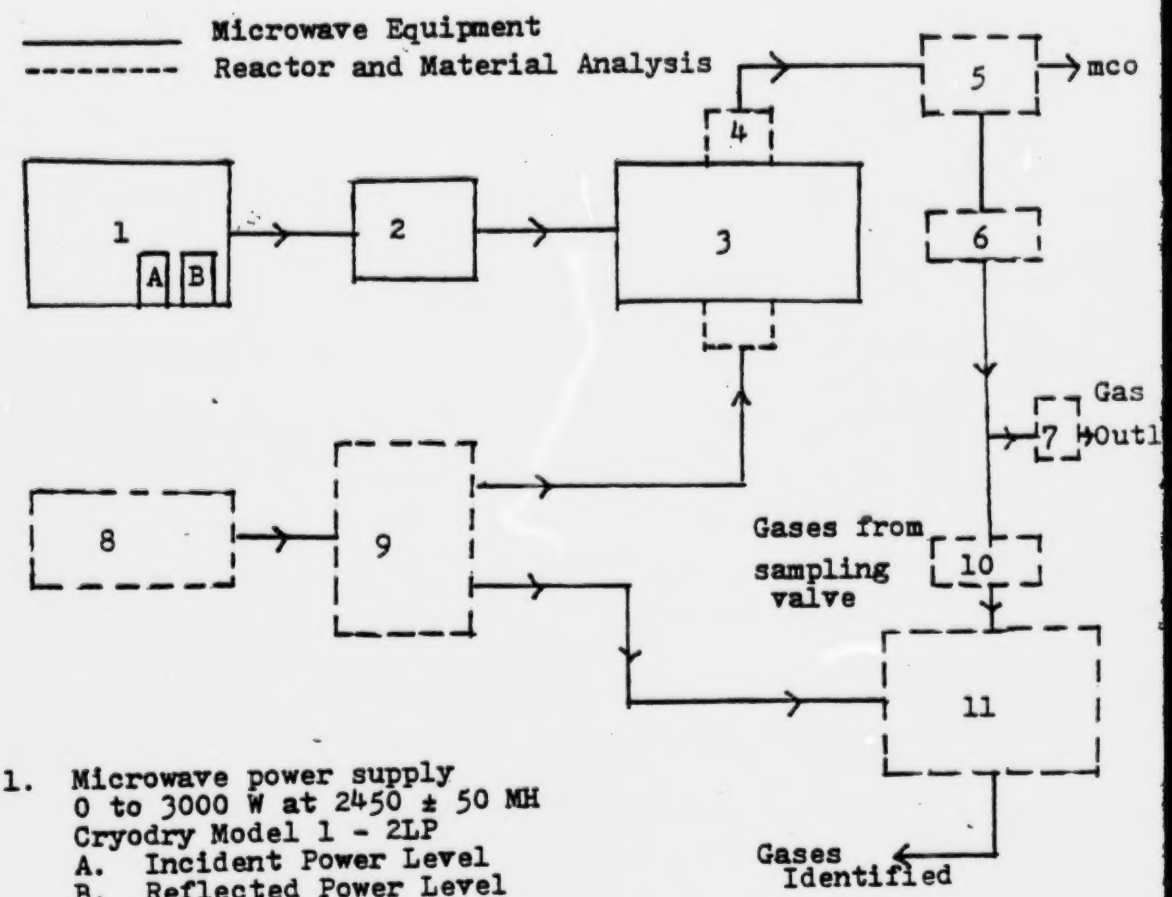
At this point, the control power switches of the Power Applicator and Power Generator were turned on. This activated

the cooling water system for the microwave power supply. The microwave power switch was then turned on and the incident power level adjusted to 100W. As soon as the microwave power was switched on, a stop-watch for timing the heating process was started. Beginning at times between 30 seconds and 2 minutes, samples of the released gases were passed through the Gas Chromatograph using the sampling valve and a 2 cc sampling loop. For all tests the chart recorder speed was set at 1 inch/minute. The sampling procedure was as follows: the place on the chart paper was marked as soon as the valve was turned to the left and the reaction time was recorded. This signified that the gases were beginning to enter the Chromatograph column. The valve was left in this position for 15 seconds to ensure that all the gas was removed from the sample loop and then it was turned back to the right so that the loop could be refilled. A series of 5 to 10 gas samples were taken over a period of about 16 minutes. The last sample was taken when no more peaks were visible on the recorder.

The above procedure was repeated for various samples which were numbered according to the place in which they were retrieved. The data was used to determine the gases released and how the amount of each gas changed as a function of time. By weighing the sample after completion of the test, an estimate of the amount of bitumen extracted could be determined.

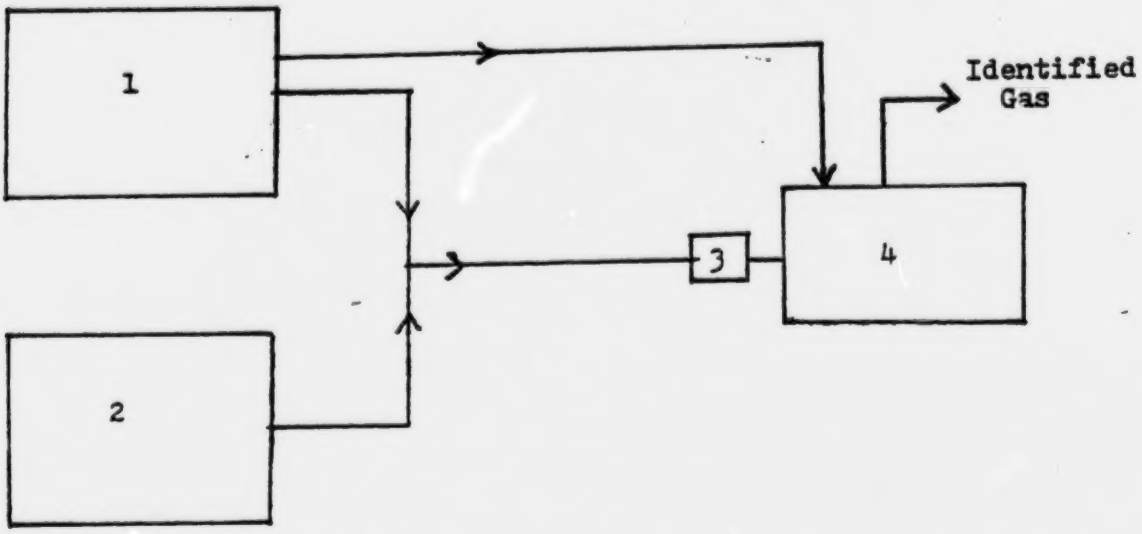
4-(c) Test Procedure II

The effect of reaction time on the percent of extracted bitumen was studied by preparing several samples from the same area and heating them for various amounts of time. From this information plots of percent bitumen extracted versus reaction time were constructed. Procedure was the same as under Test Procedure I with the exception that the quartz reactor was not connected to the line to the Gas Chromatograph. The samples were weighed after reaction times ranging from 2 to 20 minutes.



1. Microwave power supply
   0 to 3000 W at 2450 ± 50 MH
   Cryodry Model 1 - 2LP
   A. Incident Power Level
   B. Reflected Power Level
2. Microwave Circulator
3. Waveguide Cavity
4. Quartz Reactor Tube
5. Cold Trap
6. Glass Wool Filter
7. Pressure Release Valve
8. Helium Gas Bottle
9. Rotameter Tube Bank 601
   603
10. Gas Sampling Valve, with
    2 cc Sample Loop
11. Gas Chromatograph: Gow Mac
    Series 550 Thermal
    Conductivity Detector.

FIGURE I - BLOCK DIAGRAM OF REACTOR CIRCUIT



1. Helium gas cylinder
2. Gas cylinder to be analyzed (CO_2,CO,CH_4,C_2H_2, C_2,H_4,C_2H_6)
3. Sampling Valve and 2 cc sample loop
4. Gas Chromatograph

FIGURE 2 - CALIBRATING THE GAS CHROMATOGRAPH

5. PRESENTATION AND DISCUSSION OF RESULTS

Once the tests were completed the data was put into tables and all necessary calculations were performed. The results of the tests conducted for the period February 25 to March 26, 1982 are presented in the Appendix of this report. All important findings are summarized in Tables I through 4 inclusive.

In the following discussion each graph and table will be discussed as to its origin and significance. As was the case with the procedure, the discussion will be divided into three sections. The first pertains to the initial work needed to calibrate the Gas Chromatograph. This will be followed by a discussion of the Gas Chromatographic analysis for each sample tested. Contained in this section will also be a comparison of oil yields with Fischer Assay results. In the final section the effects of reaction time on the percentage of bitumen extracted will be discussed.

Section I: The Gas Chromatograph

Before actual testing began, the Gas Chromatograph was calibrated for both retention time and volume using the various gases expected to be present in the shale oil.

Results of the retention times of each gas are presented in Table A1-1 of Appendix A1.

Calibration for a specific volume was performed by injecting known volumes into the Gas Chromatograph. The results of these tests are contained in Table A1-2 of Appendix A1. These results show an essentially linear relationship between peak height and volume as shown on the plots of Peak Height versus Volume injected on Pages 31-32 .

Section II: Results of Gas Analysis

(i) The results of the Gas Chromatographic analysis for each sample analyzed are presented in Tables A1 to A7 of Appendix A2. These results are depicted graphically on Pages 35-54 . The graphs give one a good indication of how the volume of each gas produced varies over the life of the reaction process. Methane shows the most consistent behavior from sample to sample. In all cases the amount of methane produced increases rapidly for the first two to eight minutes of the reaction time. Once the volume reaches a maximum, it then drops off quickly. Acethylene exhibits the same type of behavior when present, although the time at which it reaches a maximum varies substantially and it is not found over the entire reaction period.

The profile of the volume of carbon dioxide is very inconsistent. In samples A6-01 and A7-12 it behaves much like methane, increasing in volume rapidly. In samples A2-07 and A1-07 its profile ressembles that of carbon monoxide, reaching a maximum very slowly and then tailing off to zero. In still

others, like sample A1-05 it exhibits a double maximum.

With the exception of the two cases just mentioned, the volume profile of carbon monoxide is very different from those of all other gases. Its volume increases very slowly reaching a maximum only during the latter stages of the reaction. This would seem to indicate that carbon monoxide is formed in greater quantities only when not enough oxygen is present to enable the complete oxidation of the hydrocarbons to carbon dioxide.

The two other gases present, ethylene and ethane also show little consistency between the samples tested. In all cases, however, these gases are present for only a small fraction of the total microwave reaction time.

The geographic origin of each sample tested along with a brief physical description are presented in Table I.

The total amounts of each gas released are presented in Table 2 on Page 22. Analysis has shown that the gases, carbon monoxide, methane, carbon dioxide and ethylene are present in all samples. Small amounts of acethylene and ethane were identified in some of the samples. With the exception of samples A10-03 and A7-12 the volume of carbon dioxide exceeds

that of all other gases produced. This is probably a result of combustion of the hydrocarbons released during the heating process. This is evident by the observation of a bright blue flame during the heating of the samples.

Samples injected into the Gas Chromatograph after reaction times of 30 seconds to 1 minute did not reveil any gaseous products. This would seem to indicate that there was a time delay at the start of each heating test before any significant amount of gas is released from the sample being heated. During the testing procedure, the first sign of gases being released was a yellowish-grey smoke after only 15-20 seconds of reaction time. This can account for part of the delay. The remaining portion can be attributed to the travelling time associated with going from the reactor vessel of the sample loop.

(ii) Comparison with Fischer Assay Results

Table 3 shows a comparison between the results of the microwave tests and those determined by a Fischer Assay. The latter procedure is a standardized testing method for determining the oil content of oil shale. The Fischer Assays were performed by the New Brunswick Research and Productivity Council.

The total weight losses for all samples tested by the microwave procedure were higher than those for the same samples

tested by the Fischer Assay technique. This is due solely to the significantly greater quantity of gas prodoced by the microwave reactor method. The gas yield ranged from a low of 1.12 times to a high of 11.3 times that for the Fischer Assays. The reason for such high gas yields was the reaction temperature is approximately twice that used in the standardized technique. By reducing the temperature, it would be possible to reduce the gas yield and increase the oil yield as shown by results found in Reference (3).

It can be seen from Table 3 that the moisture content in the Fischer Assay samples was greater in all cases except for sample A2-07. This can be attributed to the fact that these samples are pulverized as they exist when taken from the ground whereas the samples used in the microwave process were specially prepared, cut and dried. It must be noted, however, that the water yields for the microwave tests were determined by drying similar samples in an oven and determining the weight loss.

The oil yield by the microwave process averaged 88.8% of the Fischer Assay yield. If one considered the fact that conventional processes, like the one being used to recover oil from the tar sands of Alberta, have a recovery rate of approximately 73% this would seem to indicate the production of shale oil by heating with microwaves could be a viable operation.

Before such a statement can be made, one must examine the problem from an overall energy consideration. That is, just how much microwave power is required to recover a specified amount of energy in the form of petroleum and combustible gases. This problem was considered briefly but an in-depth study was beyond the scope of this paper.

The results obtained from two calculations were substantially different. Based on the actual amount of microwave energy used and the amount of energy in the oil recovered in the laboratory experiment, the process required over four times the energy in the oil and gas to recover these products. This can be attributed to the system design, which limited the volume of sample heated to a small fraction of the total waveguide cavity volume.

A more detailed calculation based on the same recovery rates and 100% efficiency of energy utilization showed that theoretically, 10 times the energy required to heat the shale can be recovered in the form of oil and gas. It must be noted, however, that this calculation required assumptions for the heat capacities of the shale, gas and oil and the amount of energy needed to crack the oil.

Both of these calculations are presented in detail in Appendix A4.

Section III - Effects of Reaction Time on the Percentage of Bitumen Extracted.

Results of the tests to determine the percentage of bitumen as a function of reaction time are summarized in Table 4 on Page 24. Plots of percentage by weight of extracted bitumen versus reaction time were constructed from these results and are presented in Appendix A3.

For the samples tested, results exhibit a very consistent behavior. Weight loss was very rapid during the initial stages of the reaction period. The length of time this initial stage lasted was generally related to the oil content of the samples being heated. The higher the Fischer Assay oil yield, the longer the length of this initial period. After the end of this stage, the percentage extracted changes very little over the remaining reaction time.

The total weight losses after a minimum reaction time of 16 minutes ranged from a low of 6.18% for the Albert County sample A4 to a high of 38.37% for the rich Colorado sample A1-03. Results of weight bases for samples taken from the same area show a good degree of reproducibility. Total weight losses for samples A3-04 and A3-17 were 16.28% and 16.54%, respectively. These also compare quite closely to the value of 16.06% obtained for sample A3-06 during the tests in which a gas analysis was performed.

The form of behavior exhibited by all samples was in agreement with tests performed on Athabasca Tar sand samples using the microwave cooking technique as found by Bosisio et al (2).

TABLE I - SAMPLE GEOGRAPHIC ORIGIN AND DESCRIPTION

Sample Number	Sample Origin	Description
A1	Anvil Point Mine Western Colorado	Black in color, density, 1.78 g/cm^3
A2	Anvil Point Mine Western Colorado	Slate grey in color, brittle, density 2.33 g/cm^3
A3	Surface Outcrop Frederic Brook,N.B.	Grey brown in color, soft, density 1.915 g/cm^3
A4	Surface Outcrop Frederic Brook,N.B.	Grey-black in color, very hard and not brittle, density 2.33 g/cm
A6	Surface Outcrop Frederic Brook,N.B.	Grey brown in color, soft, density 1.97 g/cm^3
A7	Surface Outcrop Frederic Brook,N.B.	Brown-Tan in color, soft and brittle, density 1.54 g/cm^3
A10	Drill Core Sample Albertite Mine Frederic Brook,N.B.	Grey-Black in color, soft, density 1.65 g/cm^3

TABLE 2 - QUANTITY OF GASES RECOVERED FOR VARIOUS SAMPLES

Gas Produced	A1-05		A1-07		A2-07		A3-06		A10-03		A6-01		A7-12	
	Vol (cm^3)	Weight (mg)	Vol (cm^3)	Weight (mg)	Vol (cm^3)	Weight (mg)	Vol (cm^3)	Weight (mg)	Vol (cm^3)	Weight (mg)	Vol (cm^3)	Weight (mg)	Vol (cm^3)	Weight (mg)
CO	31.16	38.96	21.89	27.36	3.82	4.77	40.12	50.15	160.95	201.2	26.22	32.78	66.83	83.54
CH_4	73.62	52.77	25.86	18.54	9.61	6.89	44.14	31.64	82.74	59.31	14.26	10.22	26.10	18.70
CO_2	154.6	305.6	72.76	143.8	32.68	64.60	58.58	115.8	138.6	274.0	42.22	83.46	65.08	128.6
C_2H_2	-	-	-	-	0.53	0.53	50.10	58.66	1.62	1.90	-	-	1.77	2.08
C_2H_4	14.36	19.49	11.82	16.04	1.19	1.62	25.21	34.20	114.4	155.3	6.70	9.09	3.75	5.08
C_2H_6	11.79	14.90	5.75	7.27	-	-	12.87	16.27	16.11	17.38	1.91	2.42	2.34	2.95
TOTAL	285.6	431.7	138.1	213.0	47,82	78.50	231.0	306.7	514.4	709.1	91.32	138.0	165.9	240.9
Heating Time	16.75 (min.)		15.00(min)		14.50 (min)		15.08 (min.)		16.00(min.)		17.50(min.)		16.50(min.)	

Constant Parameters: Power Level 100 Watts
Carrier Flow Rate 600 ml/min.

TABLE 3

COMPARISON OF MICROWAVE RESULTS WITH FISCHER ASSAY

SAMPLE	Total Weight Loss (%)	Oil Yield (%)	Water* Yield (%)	Gas Yield	Percentage of Fischer Assay Oil Yield Recovered
A1 Fischer Assay	26	20,4	2.1	3.5	100
A1-05 Microwave	30.44	16.19	0.34	13.91	79.4
A1-07 Microwave	31.54	19.28	2.1	10.16	94.5
A2 Fischer Assay	6.0	4.3	0.4	1.3	100
A2-07 Microwave	6.02	3.98	0.58	1.46	92.6
A3 Fischer Assay	13.0	8.2	3.1	0.64	100
A3-06 Microwave	16.06	7.32	1.49	7.25	89.3
A7 Fischer Assay	13.0	7.5	3.4	2.1	100
A7-12 Microwave	16.32	6.56	2.85	6.66	90.8
A10 Fischer Assay	26	22.4	1.4	2.1	100
A10-03 Microwave	38.63	19.25	0.93	18.45	85.9

*Note - Water Yield determined by drying a sample from the same area in an oven.

TABLE 4

PERCENTAGE BY WEIGHT OF EXTRACTED BITUMEN
VERSUS REACTION TIME FOR VARIOUS SAMPLES

Reaction Time (Minutes)	Sample Areas % by weight of extracted bitumen					
	A1-03	A2-11	A3-17	A3-04	A4	A6
2	8.46	1.86	5.72	2.86	2.35	3.63
4	13.72	3.51	8.22	4.15	5.05	5.70
6	23.38	4.37	10.94	8.61	5.33	12.01
8	31.52		13.50	11.92	5.52	12.61
10	35.66	6.21	15.69			13.65
12				14.33	6.12	13.40
15	37.55	6.34				13.46
16			15.89	15.35	6.18	
18		6.49				
20	38.37					

6. CONCLUSIONS

(1) It is possible to extract up to 94.5% of the Fischer Assay oil yield using a microwave power reactor with an energy output rate of 100 Watts.

(2) The gases released from all heated samples included carbon monoxide, methane, carbon dioxide and ethylene. Acethylene and ethane were also identified within the off gas in some cases.

(3) Gas yields from the microwave heating method were significantly higher than for the Fischer Assay Technique.

(4) For all samples tested, plots of percentage by weight of bitumen extracted as a function of reaction time exhibit the same type of behavior. This behavior is in agreement with that found by Bosisio et al (2).

7. RECOMMENDATIONS

(1) The economics of developing a commercial microwave process be investigated.

(2) Comparison be made, from an energy point of view, between the microwave process and other available extraction methods.

(3) The effects of power level and reactor temperature on gas yield be studied.

(4) Studies be made into the environmental complications that may result from such a process.

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APPENDIX A1

TABLE A1-1

CALIBRATION OF GAS CHROMATOGRAPH FOR RETENTION TIME

Parameters	Helium Flow Rate	60 cm^3/min.
	Detector Temp.	155°C
	Column Temp.	165°C
	Injection Port Temp.	200°C

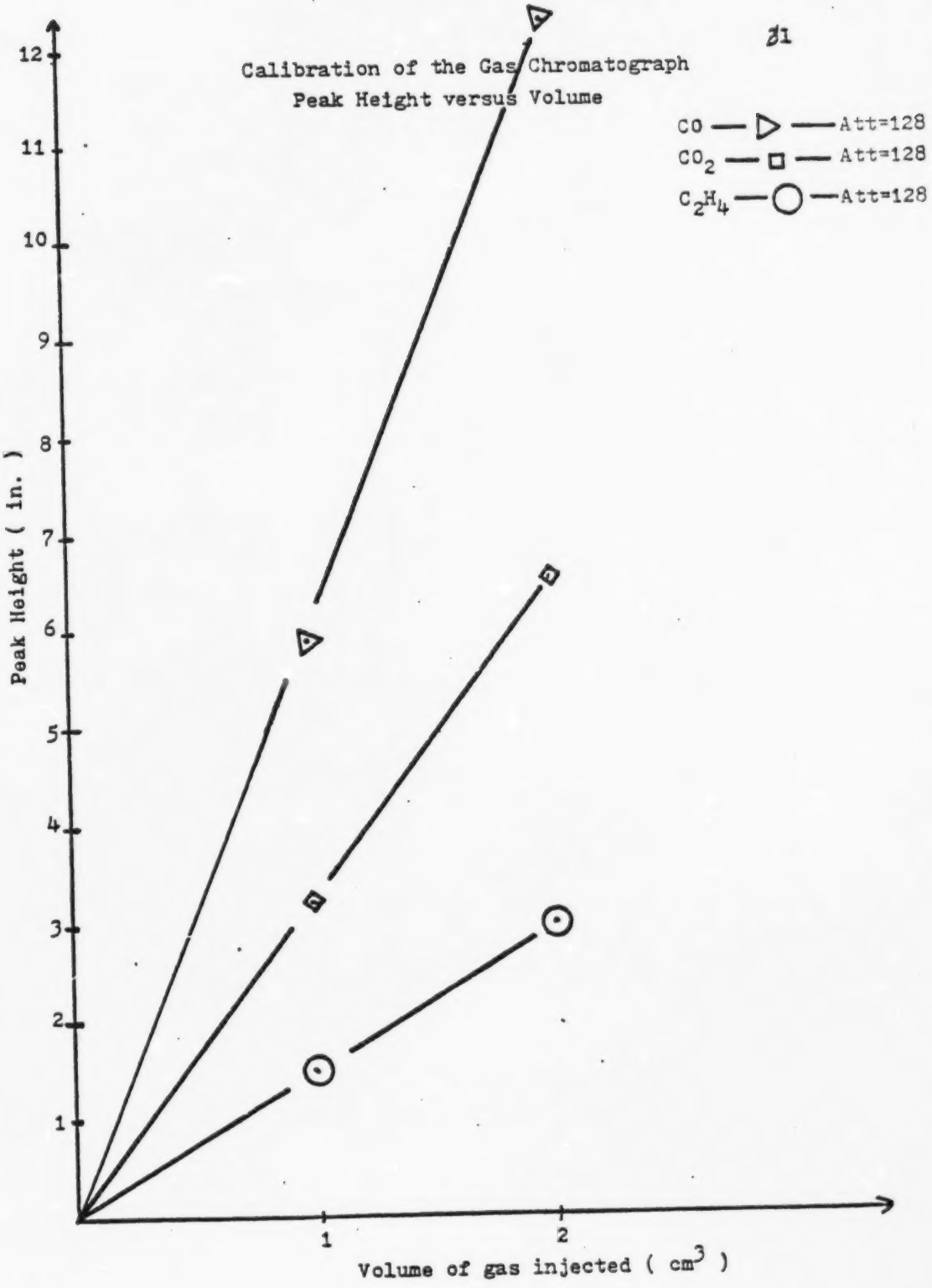
Gas	Retention Time Min. : Sec.
CO	0 : 18
CH_4	0 : 28
CO_2	0 : 42
C_2H_2	1 : 16
C_2H_4	1 : 54
C_2H_6	2:36 - 2:42

TABLE A1-2

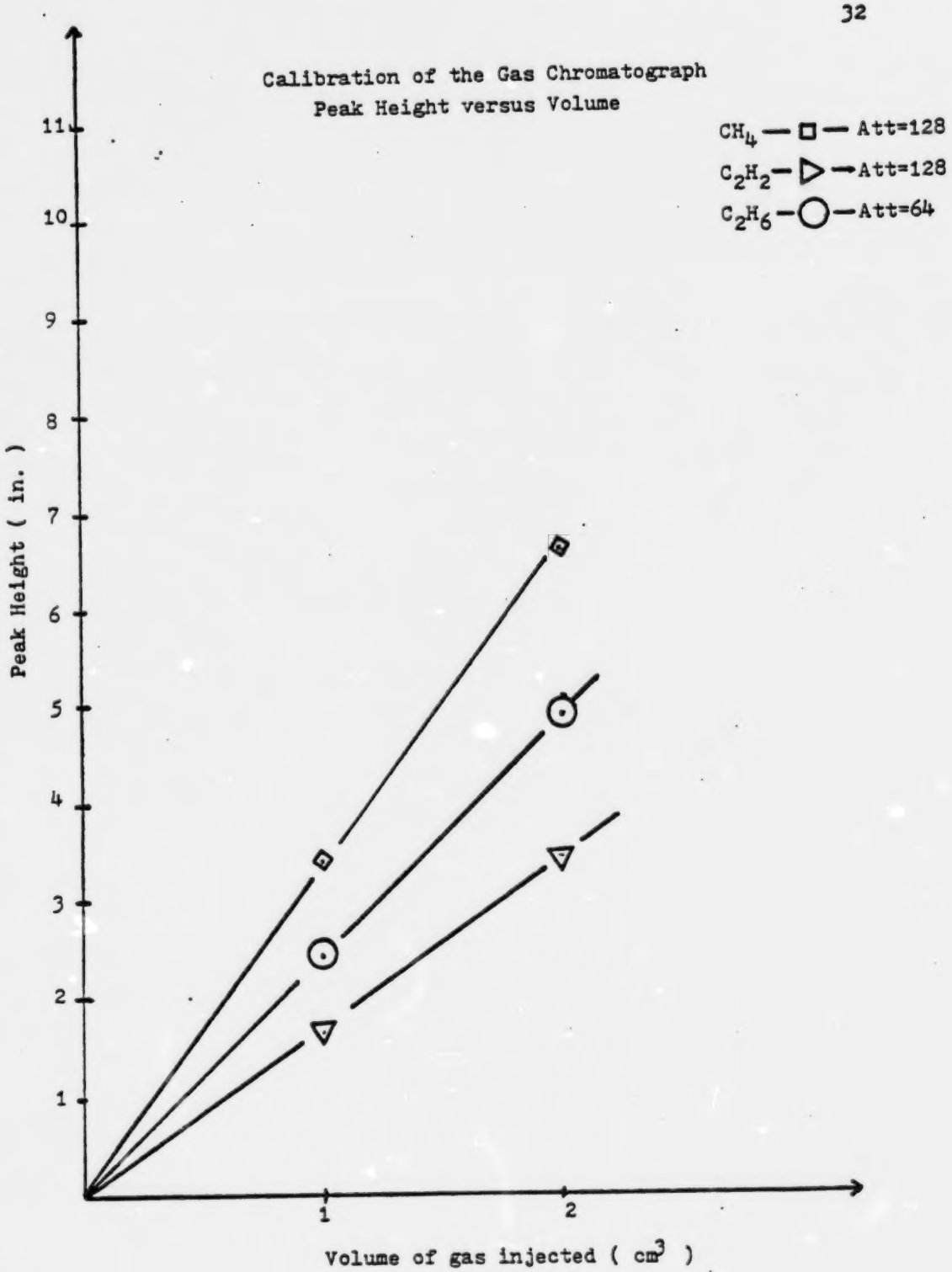
CALIBRATION OF GAS CHROMATOGRAPH FOR PEAK HEIGHT OF GAS VERSUS VOLUME OF THAT GAS INJECTED

Note: Attenuation Valve in brackets

Gas	Peak Height (in.) for 1 cm^3 Loop		Peak Height (in.) for 2 cm^3 Loop	
CO	5.9	(128)	6.15	(256)
CH_4	6.78	(64)	6.6	(128)
CO_2	6.5	(64)	6.55	(128)
C_2H_2	3.3	(64)	3.45	(128)
C_2H_4	2.95	(64)	3.0	(128)
C_2H_6	4.9	(32)	4.9	(64)


Calibration of the Gas Chromatograph
Peak Height versus Volume
CO — Att=128
CO_2 — Att=128
C_2H_4 — Att=128
Peak Height (in.)
12
11
10
9
8
7
6
5
4
3
2
1
1
2
Volume of gas injected (cm^3)

Calibration of the Gas Chromatograph
Peak Height versus Volume



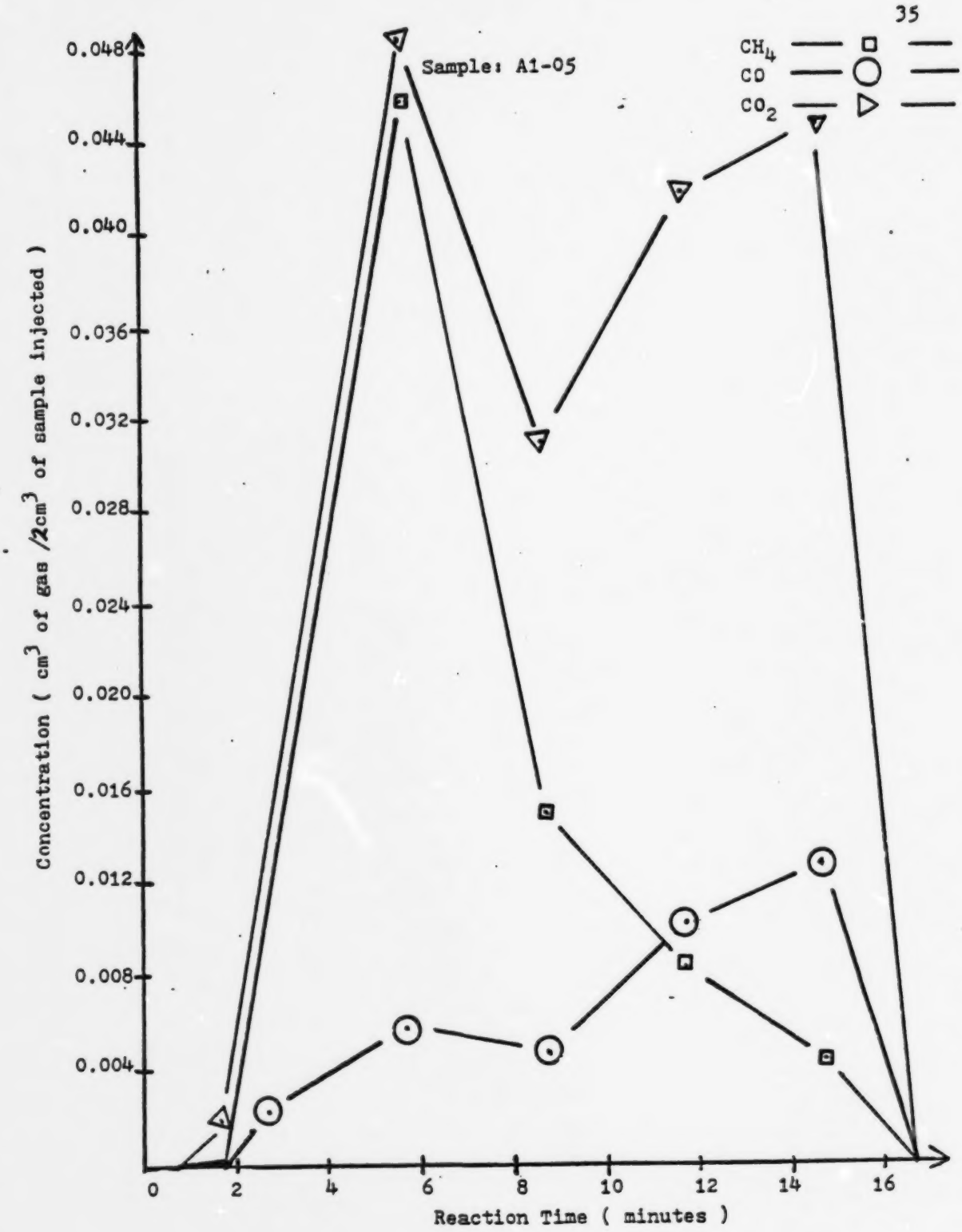
APPENDIX A2

TABLE A1

RESULTS OF GAS ANALYSIS FOR SAMPLE A1-05

SAMPLE WEIGHT 3.1029 grams

Reaction Time (min.)	Gases Released Expressed as a concentration $cm^3 \times 10^2$ /2 cm^3 of sample injected and % respectively					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
0.75	-	-	-	-	-	-
	-	-	-	-	-	-
1.75	0.0254	0.0473	0.193	-	-	-
	9.63	17.94	72.43	-	-	-
2.75	0.279	1.278	1.756	-	0.521	0.510
	6.42	29.42	40.43	-	11.99	11.74
5.75	0.610	4.59	4.87	-	0.739	0.319
	5.48	41.24	43.77	-	6.64	2.87
8.75	0.498	1.52	3.12	-	0.396	0.485
	8.27	25.25	51.84	-	6.58	8.06
11.75	1.06	2.828	4.20	-	0.114	0.166
	16.65	13.00	65.95	-	1.79	2.61
14.75	1.32	0.450	4.51	-	-	-
	21.02	7.16	71.82	-	-	-
16.75	-	-	-	-	-	-
	-	-	-	-	-	-


Sample: A1-05
CH_4
CO
CO_2
0.048
0.044
0.040
0.036
0.032
0.028
0.024
0.020
0.016
0.012
0.008
0.004
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

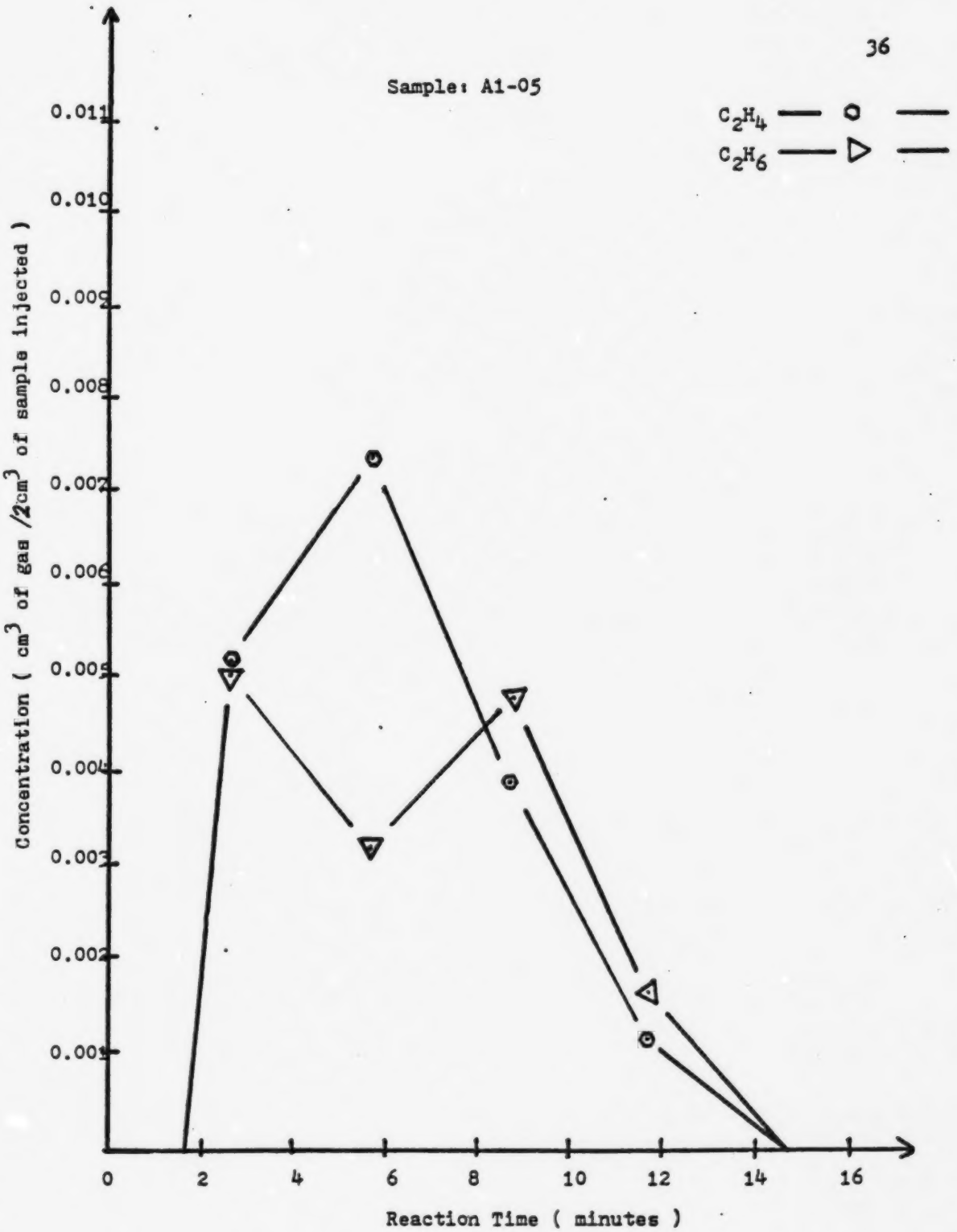
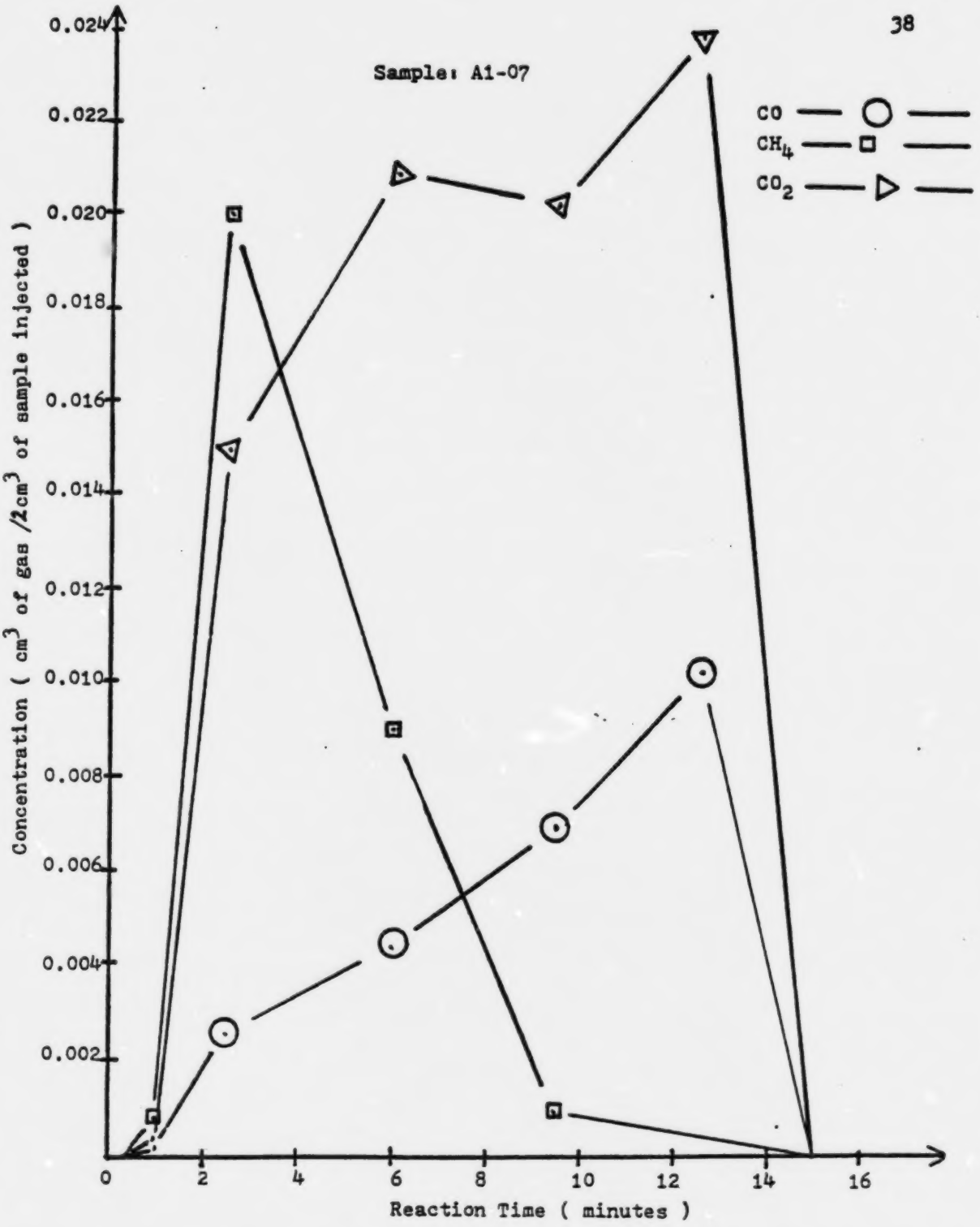

Sample: A1-05
C_2H_4
C_2H_6
Concentration (cm^3 of gas /2cm^3 of sample injected)
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

TABLE A2

RESULTS OF GAS ANALYSIS FOR SAMPLE A1-07

SAMPLE WEIGHT 2.0963 grams

Reaction Time (min.)	Gases Released Expressed as a concentration $cm^3 \times 10^2$ /2cm^3 of sample injected and % respectively.					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
0.50	-	-	-	-	-	-
	-	-	-	-	-	-
1.00	0.0115	0.0284	0.0763	-	-	-
	13.61	23.43	62.95	-	-	-
2.30	0.254	1.99	1.50	-	1.14	0.516
	4.70	36.85	22.78	-	21.11	9.56
6.00	0.440	.904	2.09	-	0.312	0.179
	11.31	23.03	53.25	-	7.95	4.56
9.50	0.699	0.0994	2.02	-	-	-
	24.80	3.53	71.67	-	-	-
12.50	1.03	0.0473	2.38	-	-	-
	29.79	1.37	68.84	-	-	-
15.0	-	-	-	-	-	-
	-	-	-	-	-	-


Sample: A1-07
CO
CH_4
CO_2
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

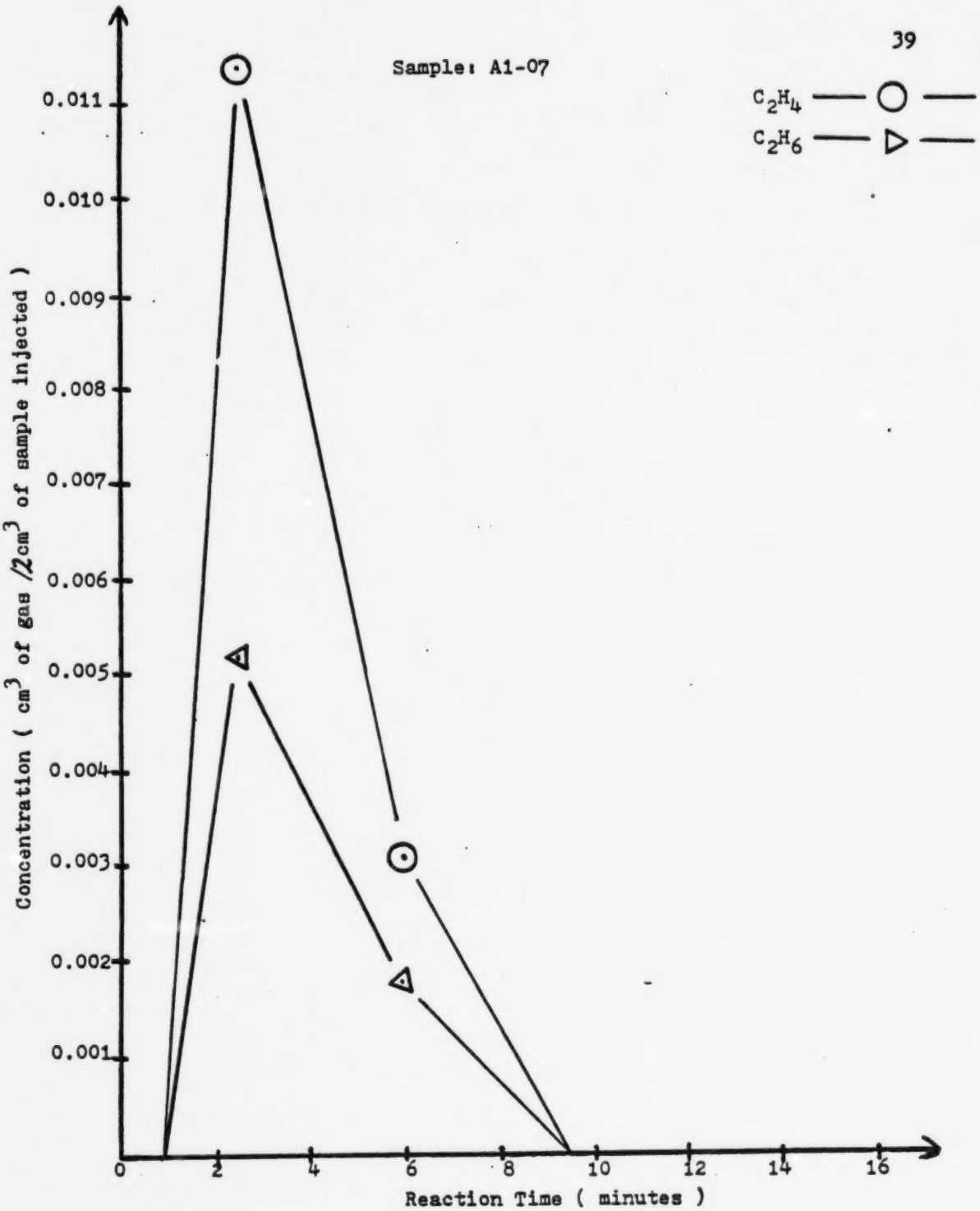
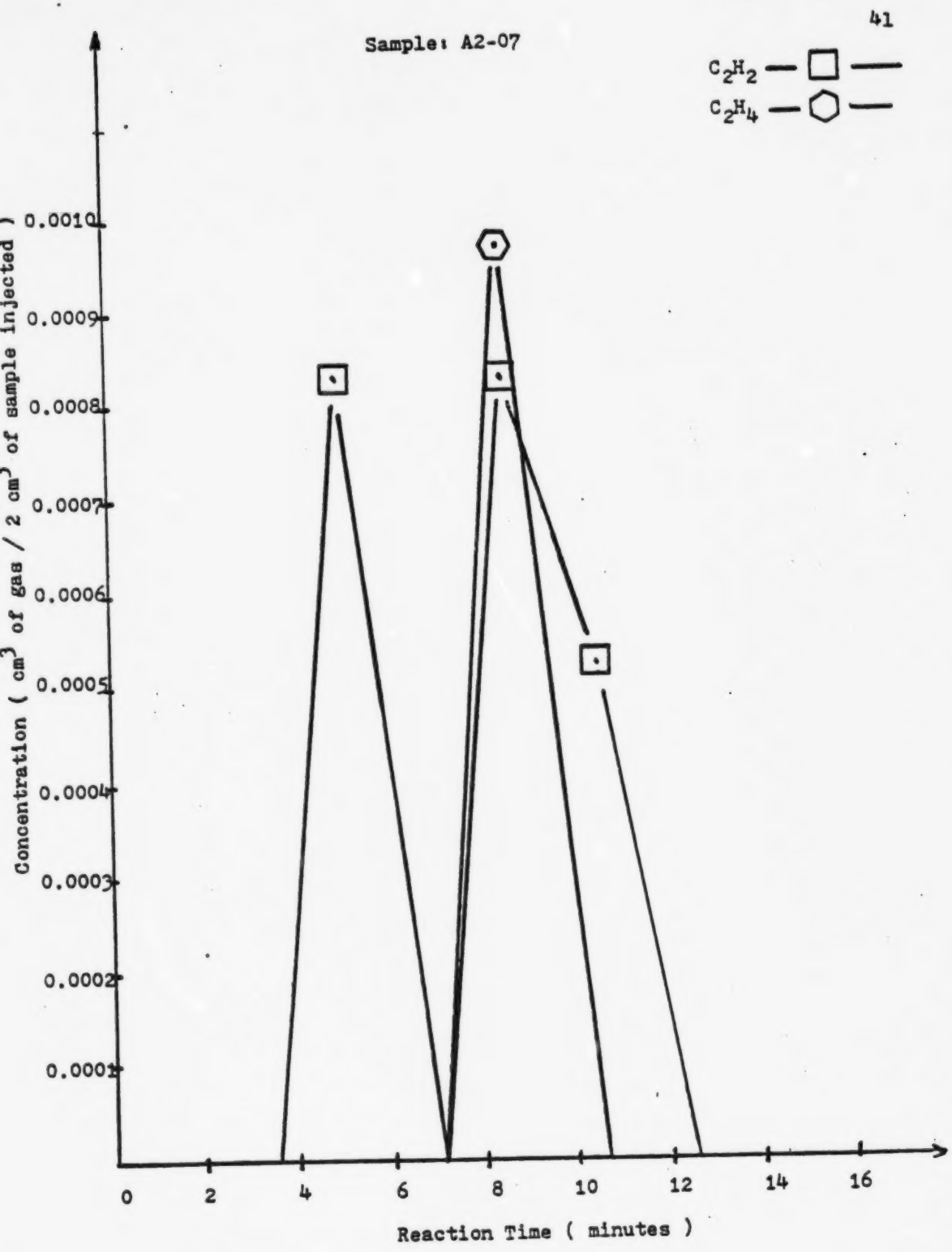

Sample: A1-07
C_2H_4
C_2H_6
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

TABLE A3

RESULTS OF GAS ANALYSIS FOR SAMPLE A2-07

SAMPLE WEIGHT 5.3844 grams

Reaction Time (min.)	Gases Released Expressed as a concentration $cm^3 \times 10^2$ /2 cm^3 of sample injected and % respectively					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
0.5	-	-	-	-	-	-
	-	-	-	-	-	-
1.50	-	-	0.0533	-	-	-
	-	-	100	-	-	-
2.50	0.0381	0.0521	0.525	-	-	-
	6.19	18.18	75.15	-	-	-
3.50	0.066	0.180	0.744	-	-	-
	6.67	18.18	75.15	-	-	-
5.00	0.0788	0.331	0.887	-	0.0833	-
	5.71	23.98	64.27	-	6.04	-
7.00	0.0788	0.379	0.954	-	-	-
	5.58	26.85	67.57	-	-	-
8.50	0.130	0.346	1.02	0.0996	0.0833	-
	7.70	20.49	60.99	5.90	4.93	-
11.50	0.142	0.298	1.03	-	.0521	-
	9.33	19.58	67.67	-	3.42	-
12.50	0.183	0.241	1.15	-	-	-
	11.63	15.31	73.06	-	-	-
14.50	-	-	-	-	-	-
	-	-	-	-	-	-


Sample: A2-07
C_2H_2
C_2H_4
Concentration (cm^3 of gas / 2 cm^3 of sample injected)
0.0010
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

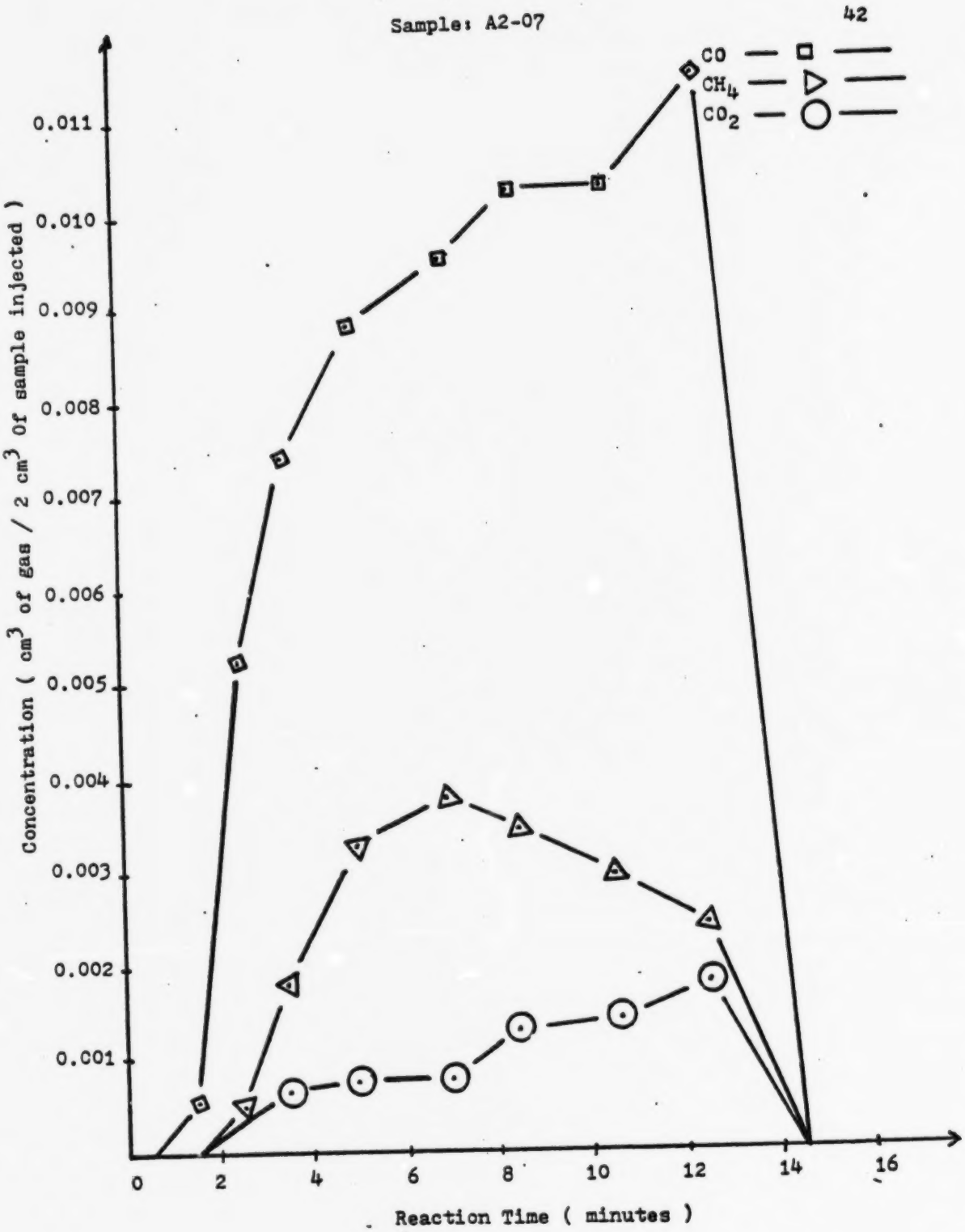
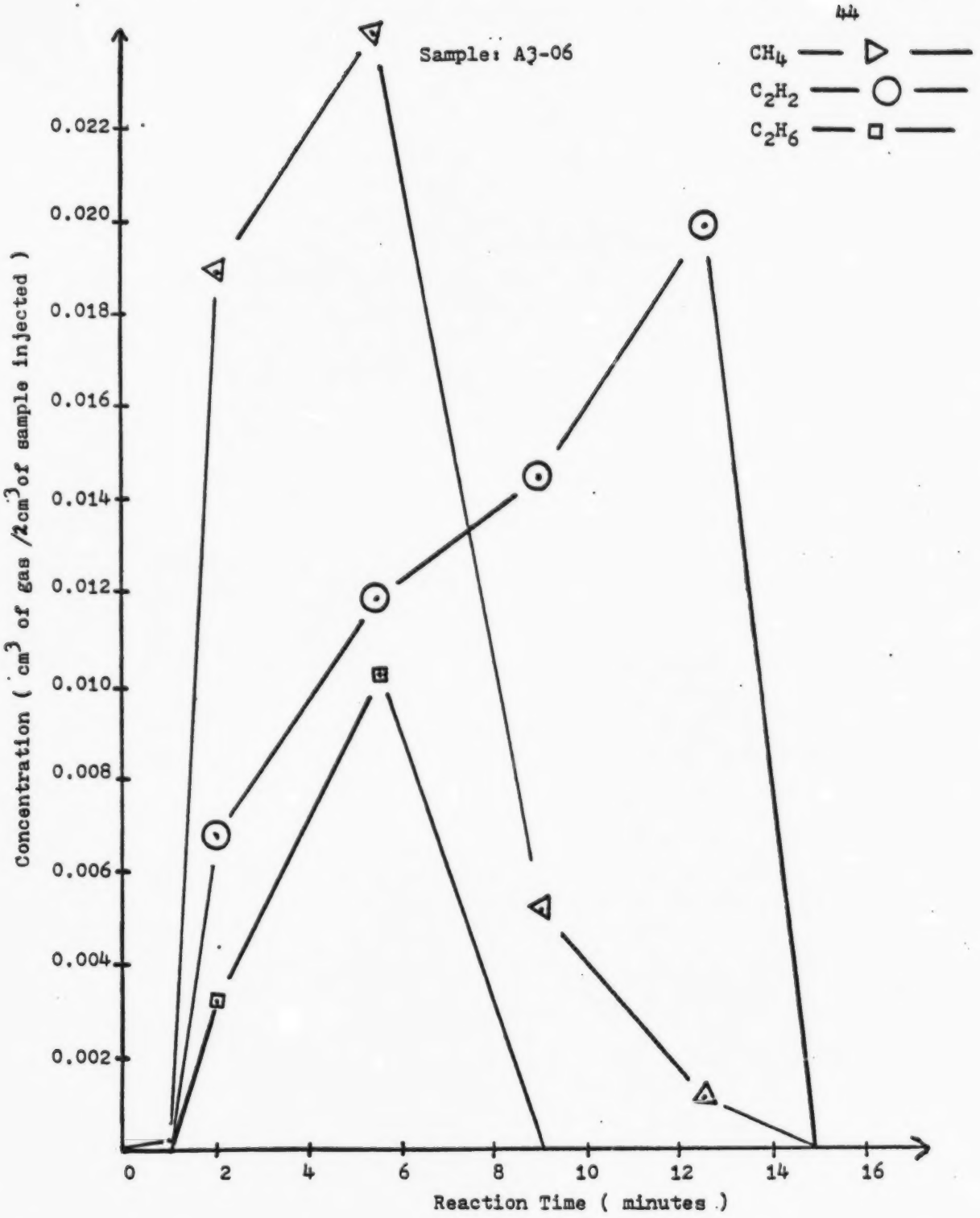

Sample: A2-07
CO
CH_4
CO_2
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
Concentration (cm^3 of gas / 2 cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

TABLE A4

RESULTS OF GAS ANALYSIS FOR SAMPLE A3-06

SAMPLE WEIGHT 4.2316 grams

Reaction Time (Min.)	Gas Released Expressed as a concentration $cm^3 \times 10^2$ /$2cm^3$ of sample injected and % respectively.					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
1.00	0.130 10.01	0.0284 2.19	1.14 87.80	- -	- -	- -
2.00	0.953 10.40	1.89 20.63	3.53 38.53	0.679 7.41	1.79 19.54	0.319 3.48
5.50	0.889 10.83	2.41 29.36	1.46 17.78	1.18 14.37	1.25 15.23	1.02 12.43
9.00	1.02 26.20	0.469 12.05	0.954 24.50	1.45 37.25	- -	- -
12.50	1.47 34.78	0.118 2.79	0.649 15.35	1.99 47.08	- -	- -
15.00	- -	- -	- -	- -	- -	- -


Sample: A3-06
CH_4
C_2H_2
C_2H_6
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

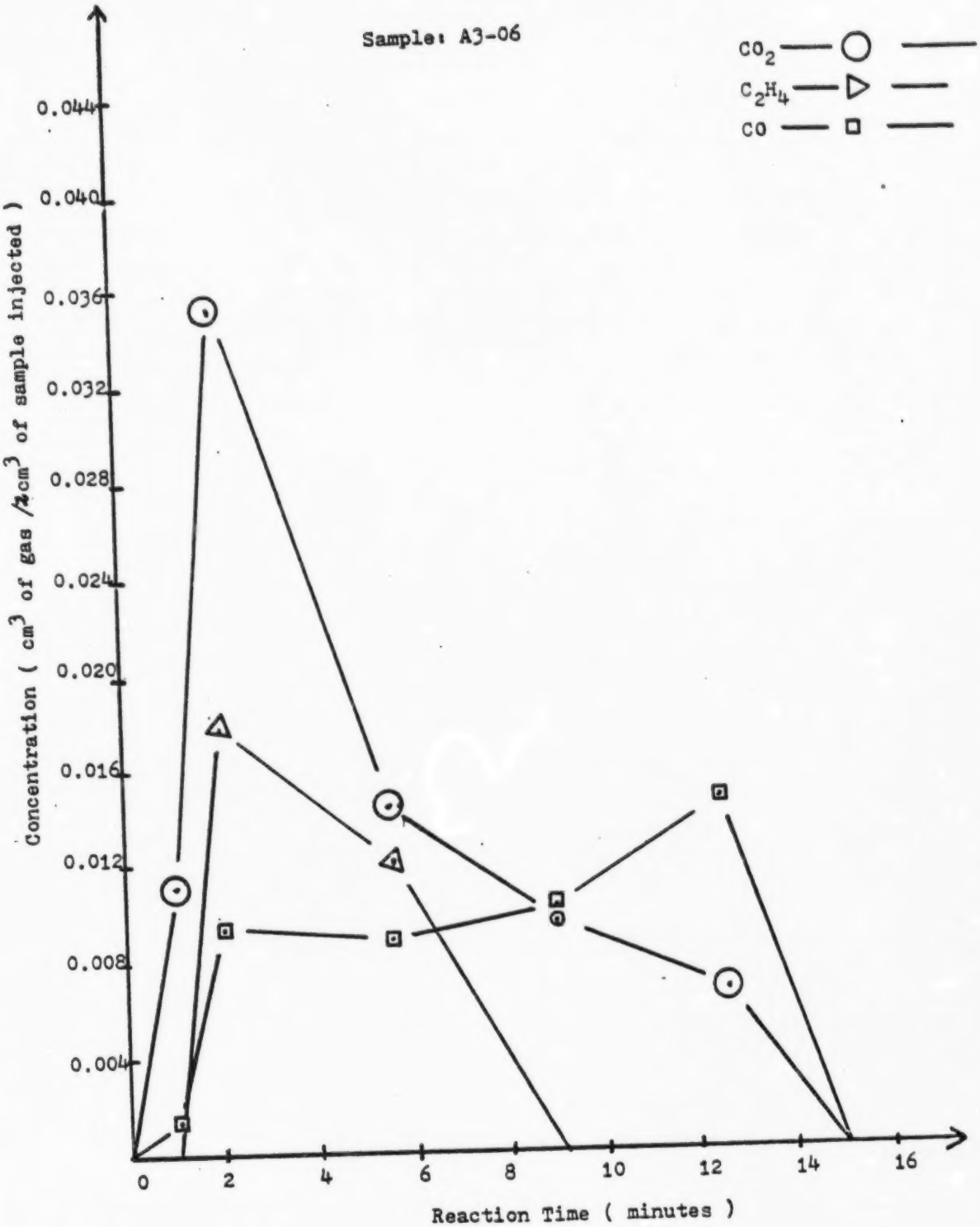

Sample: A3-06
CO_2
C_2H_4
CO
0.044
0.040
0.036
0.032
0.028
0.024
0.020
0.016
0.012
0.008
0.004
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

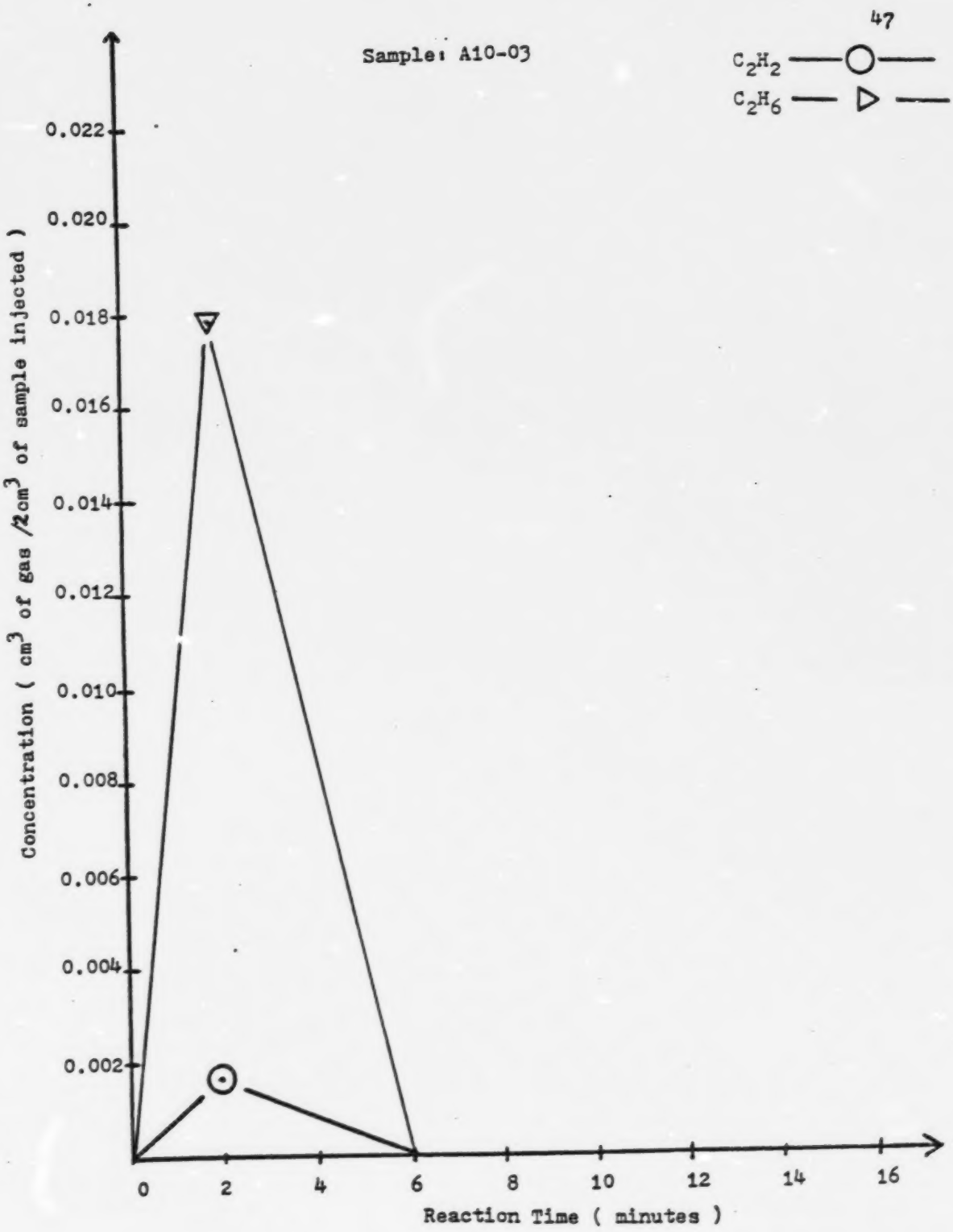
TABLE A5

RESULTS OF GAS ANALYSIS FOR SAMPLE A10-03

SAMPLE WEIGHT 3.8435 grams

Reaction Time (Min.)	Gases Released Expressed as a concentration $cm^3 \times 10^2$ /2cm^3 of sample injected and % respectively					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
2.00	1.60 6.52	7.97 32.51	3.40 13.86	0.181 0.74	9.58 39.07	1.79 7.30
6.00	10.37 52.73	0.814 4.14	7.65 38.90	- -	0.833 4.23	- -
9.00	3.13 49.09	0.189 2.96	2.14 33.56	- -	0.917 14.38	 -
13.00	0.457 23.58	0.0473 2.44	0.496 25.59	- -	0.938 48.39	- -
16.00	- -	- -	- -	- -	- -	- -

Sample: A10-03



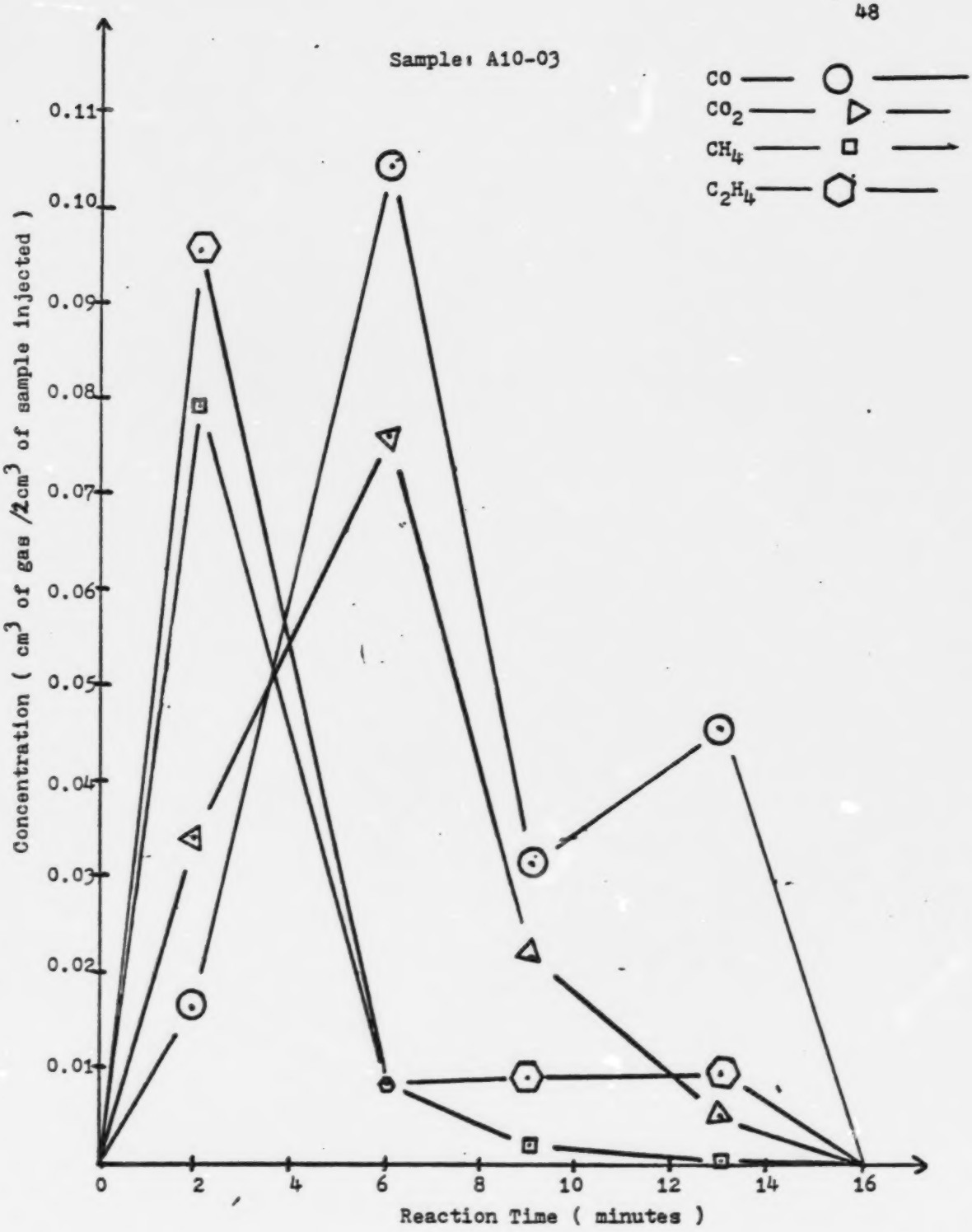
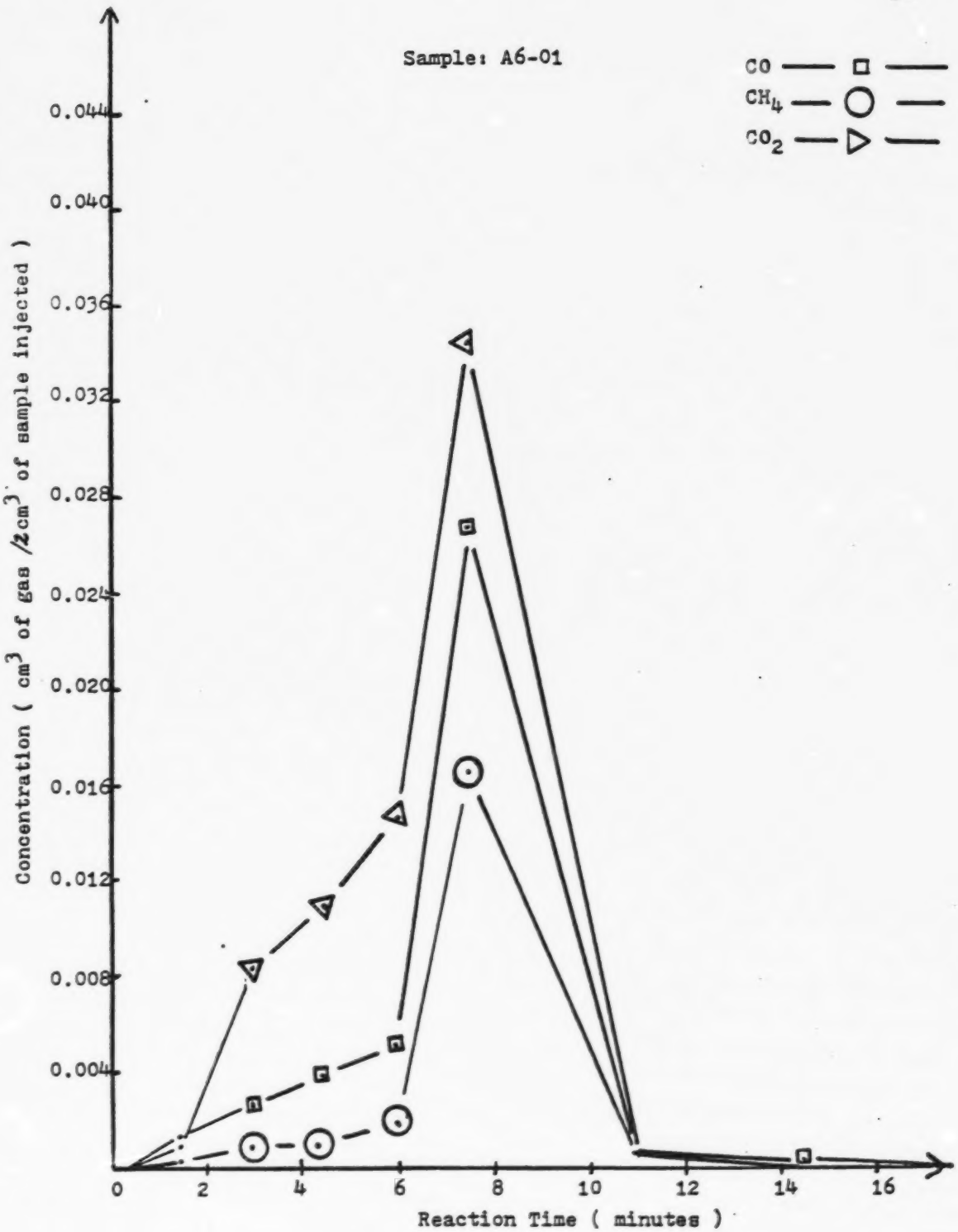

Sample: A10-03
CO
CO_2
CH_4
C_2H_4
Concentration (cm^3 of gas /2cm^3 of sample injected)
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

TABLE A6

RESULTS OF GAS ANALYSIS FOR SAMPLE A6-01
SAMPLE WEIGHT 4.8083 grams

Reaction Time (Min.)	Gases Released Expressed as a concentration $cm^3 \times 10^2$ /2cm^3 of sample injected and % respectively					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
0.50	-	-	-	-	-	-
	-	-	-	-	-	-
1.50	0.127	0.0284	0.0954	-	-	-
	50.64	11.32	38.04	-	-	-
3.00	0.264	0.0852	0.830	-	-	-
	22.39	7.22	70.39	-	-	-
4.50	0.379	0.0954	1.09	-	-	-
	24.24	6.05	69.71	-	-	-
6.00	0.506	0.180	1.48	-	-	-
	23.36	8.31	68.33	-	-	-
7.50	2.64	1.65	3.45	-	0.416	0.255
	31.39	19.62	41.02	-	4.94	3.03
11.00	0.0508	0.0237	0.0477	-	0.167	-
	17.56	8.20	16.49	-	57.75	-
14.50	0.0254	-	0.019	-	0.1875	-
	10.95	-	8.19	-	80.85	-
17.50	-	-	-	-	-	-
	-	-	-	-	-	-


Sample: A6-01
CO
CH_4
CO_2
0.044
0.040
0.036
0.032
0.028
0.024
0.020
0.016
0.012
0.008
0.004
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

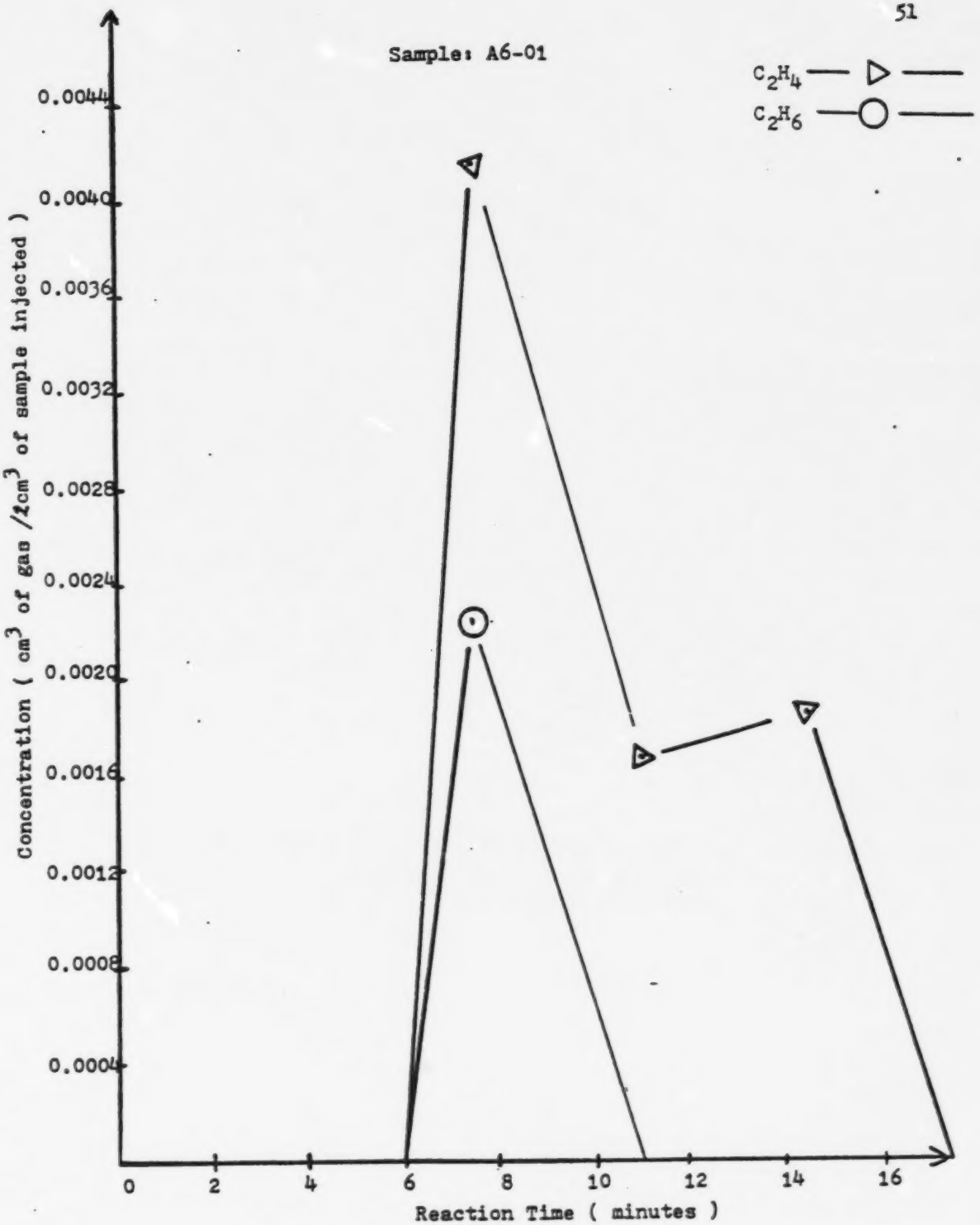
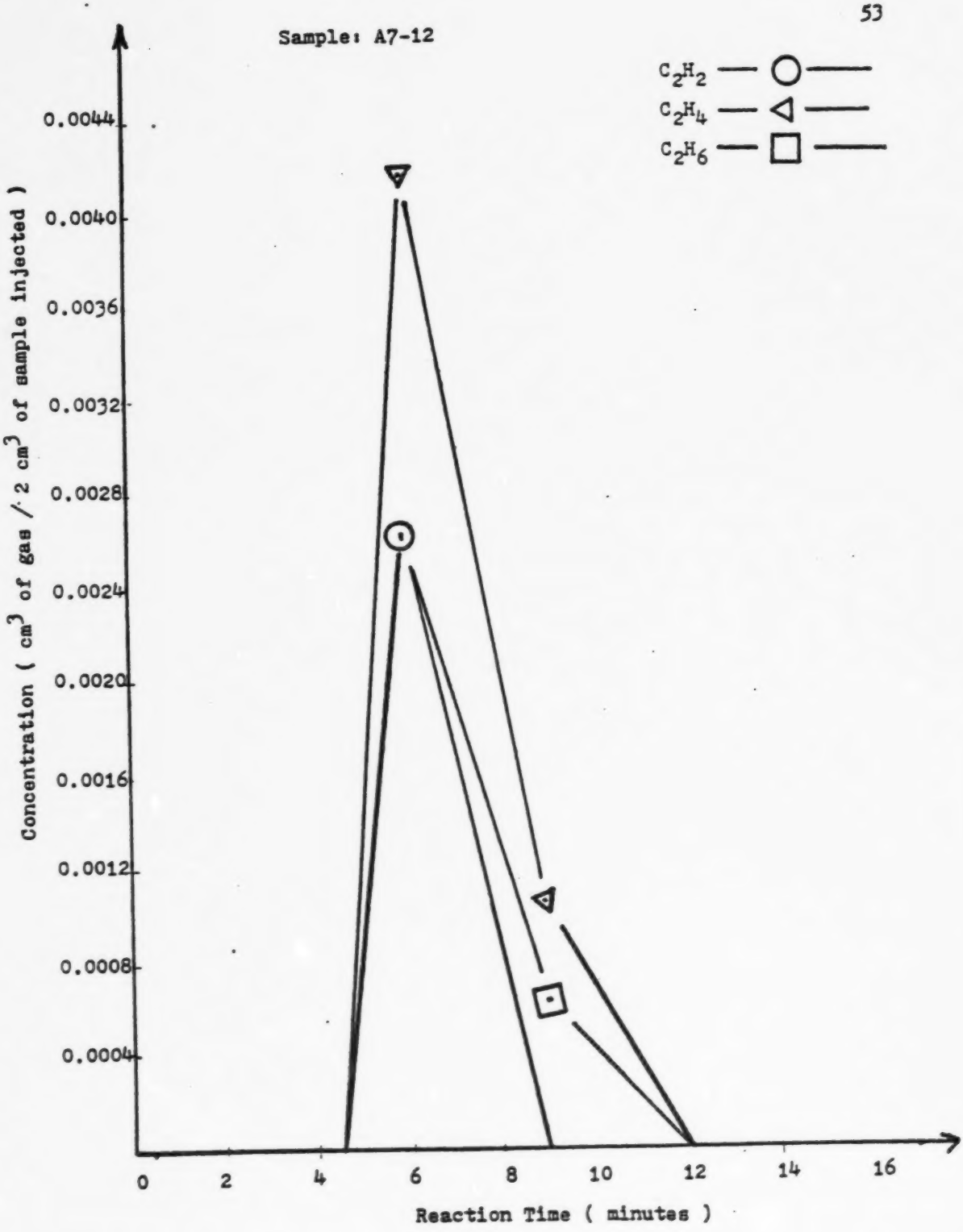

Sample: A6-01
C_2H_4
C_2H_6
Concentration (cm^3 of gas /cm^3 of sample injected)
0.0044
0.0040
0.0036
0.0032
0.0028
0.0024
0.0020
0.0016
0.0012
0.0008
0.0004
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

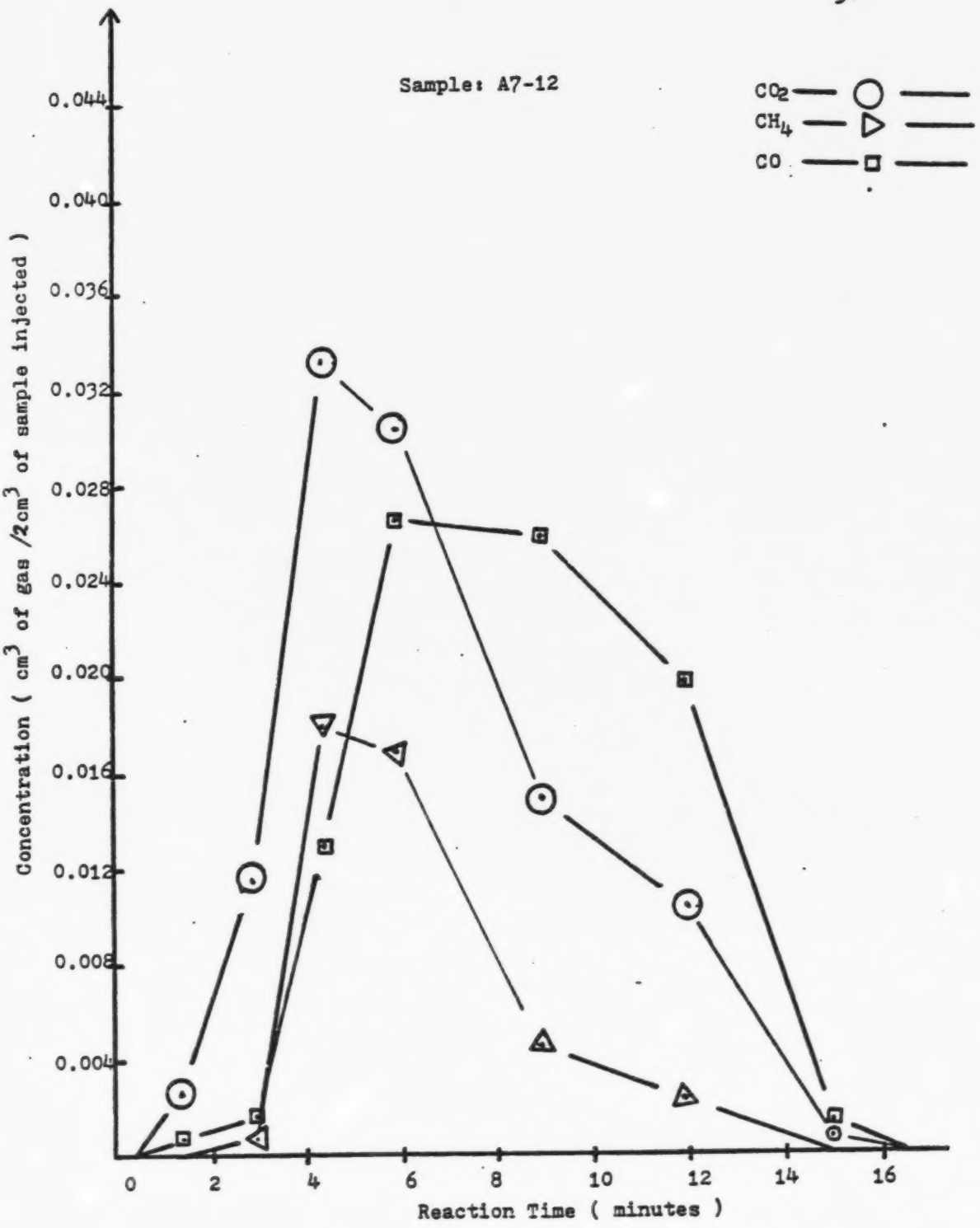
TABLE A7

RESULTS OF GAS ANALYSIS FOR SAMPLE A7-12

SAMPLE WEIGHT 3.6172 grams

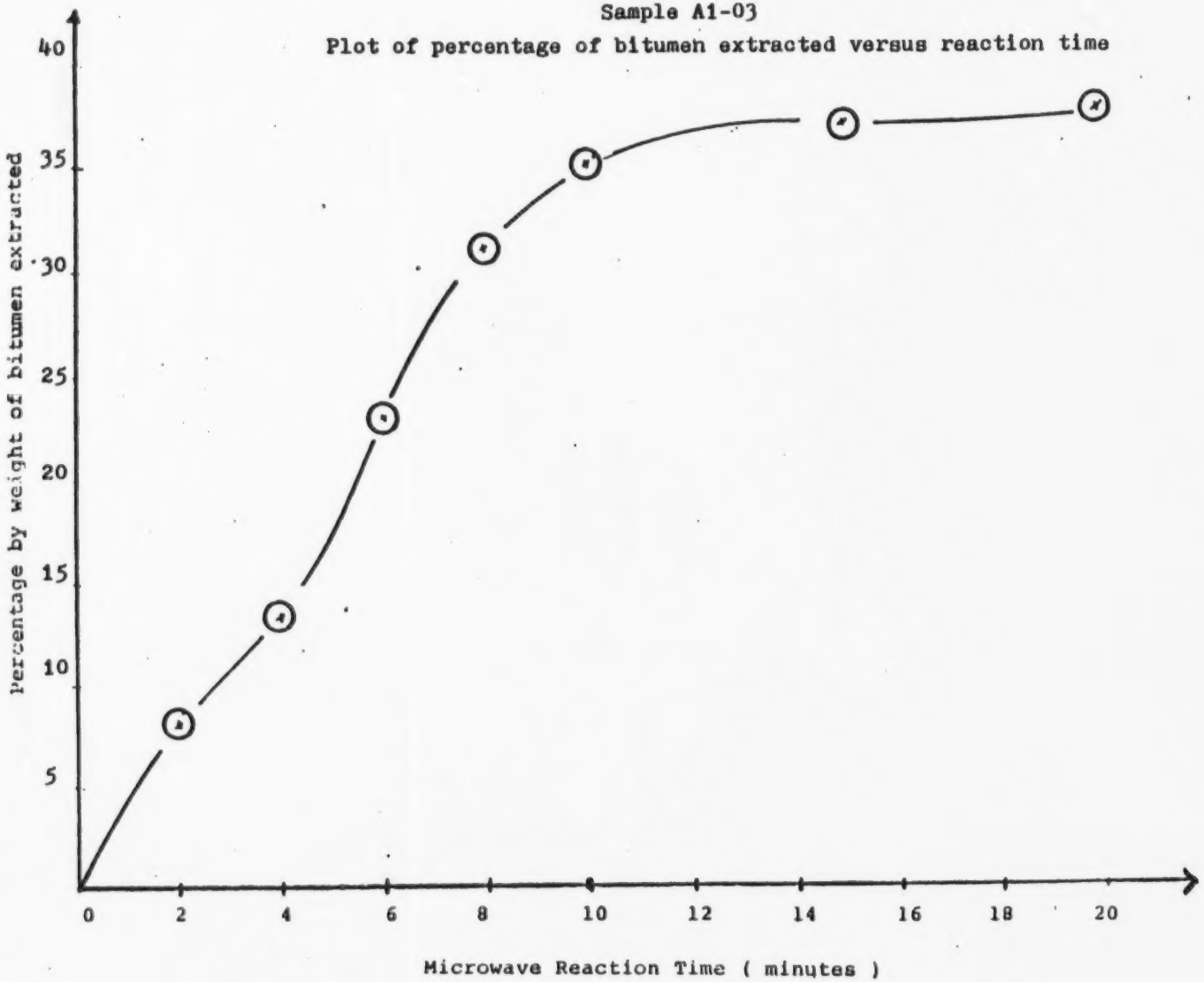
Reaction Time (Min.)	Gases Released Expressed as a concentration $cm^3 \times 10^2$ /$2cm^3$ of samples injected and % respectively					
	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_2H_6
0.50	-	-	-	-	-	-
	-	-	-	-	-	-
1.50	0.0775	-	0.2624	-	-	-
	22.80	-	77.20	-	-	-
3.00	0.147	0.710	1.14	-	-	-
	10.84	5.23	83.93	-	-	-
4.50	1.295	1.80	3.33	-	-	-
	20.17	28.00	51.83	-	-	-
6.00	2.67	1.695	3.05	0.263	0.417	0.261
	31.95	20.28	36.50	3.15	4.99	3.12
9.00	2.59	0.459	1.50	-	0.104	0.0638
	54.92	9.73	31.80	-	2.20	1.35
12.00	1.98	0.227	1.05	-	-	-
	60.79	6.97	32.24	-	-	-
15.00	0.140	0.00947	0.0668	-	-	-
	64.73	4.38	30.89	-	-	-
16.00	0.0279	-	0.0191	-	-	-
	59.36	-	40.64	-	-	-
16.50	-	-	-	-	-	-
	-	-	-	-	-	-


Sample: A7-12
C_2H_2
C_2H_4
C_2H_6
0.0044
0.0040
0.0036
0.0032
0.0028
0.0024
0.0020
0.0016
0.0012
0.0008
0.0004
Concentration (cm^3 of gas / 2 cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)


Sample: A7-12
CO_2
CH_4
CO
0.044
0.040
0.036
0.032
0.028
0.024
0.020
0.016
0.012
0.008
0.004
Concentration (cm^3 of gas /2cm^3 of sample injected)
0
2
4
6
8
10
12
14
16
Reaction Time (minutes)

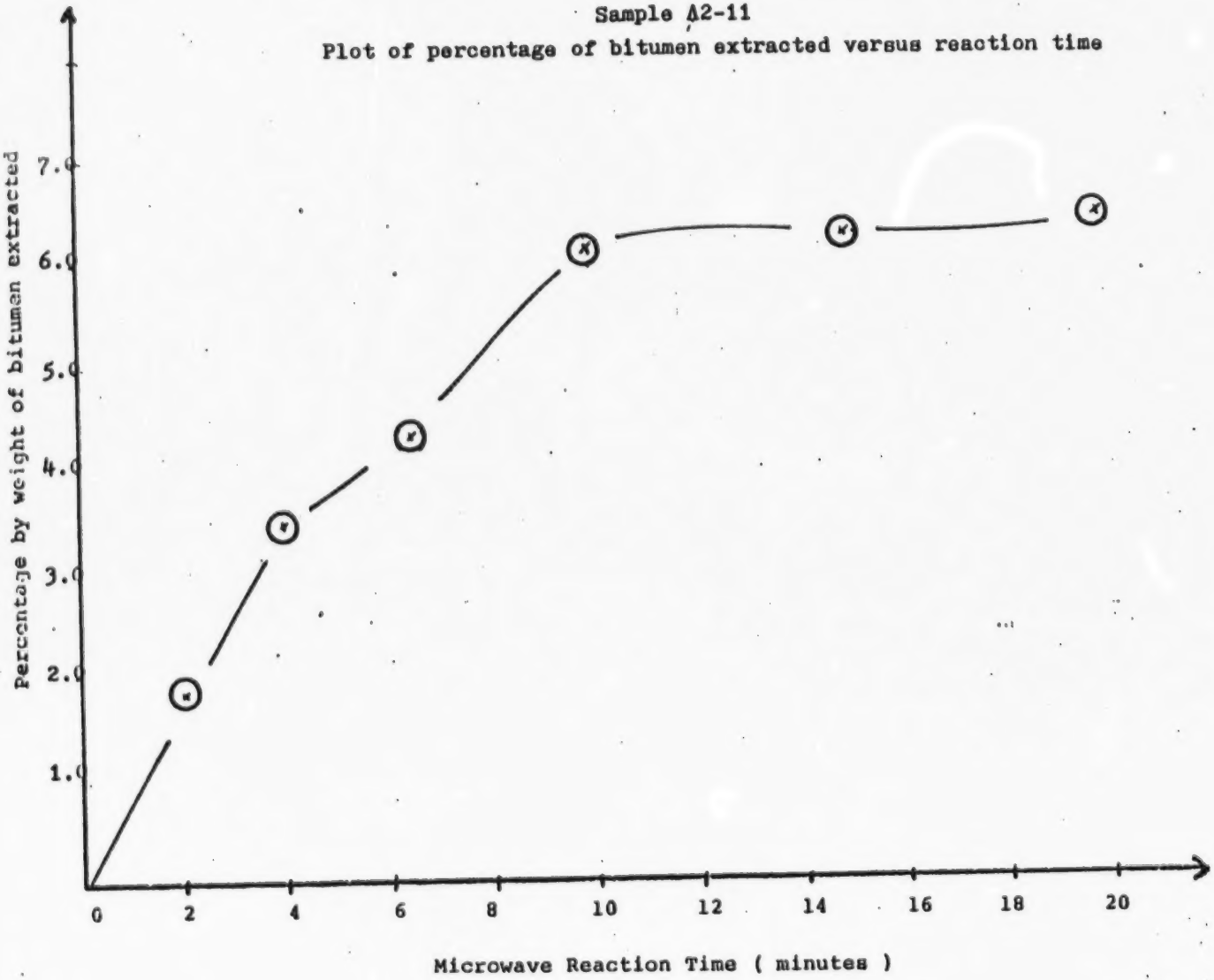
Sample A1-03

Plot of percentage of bitumen extracted versus reaction time



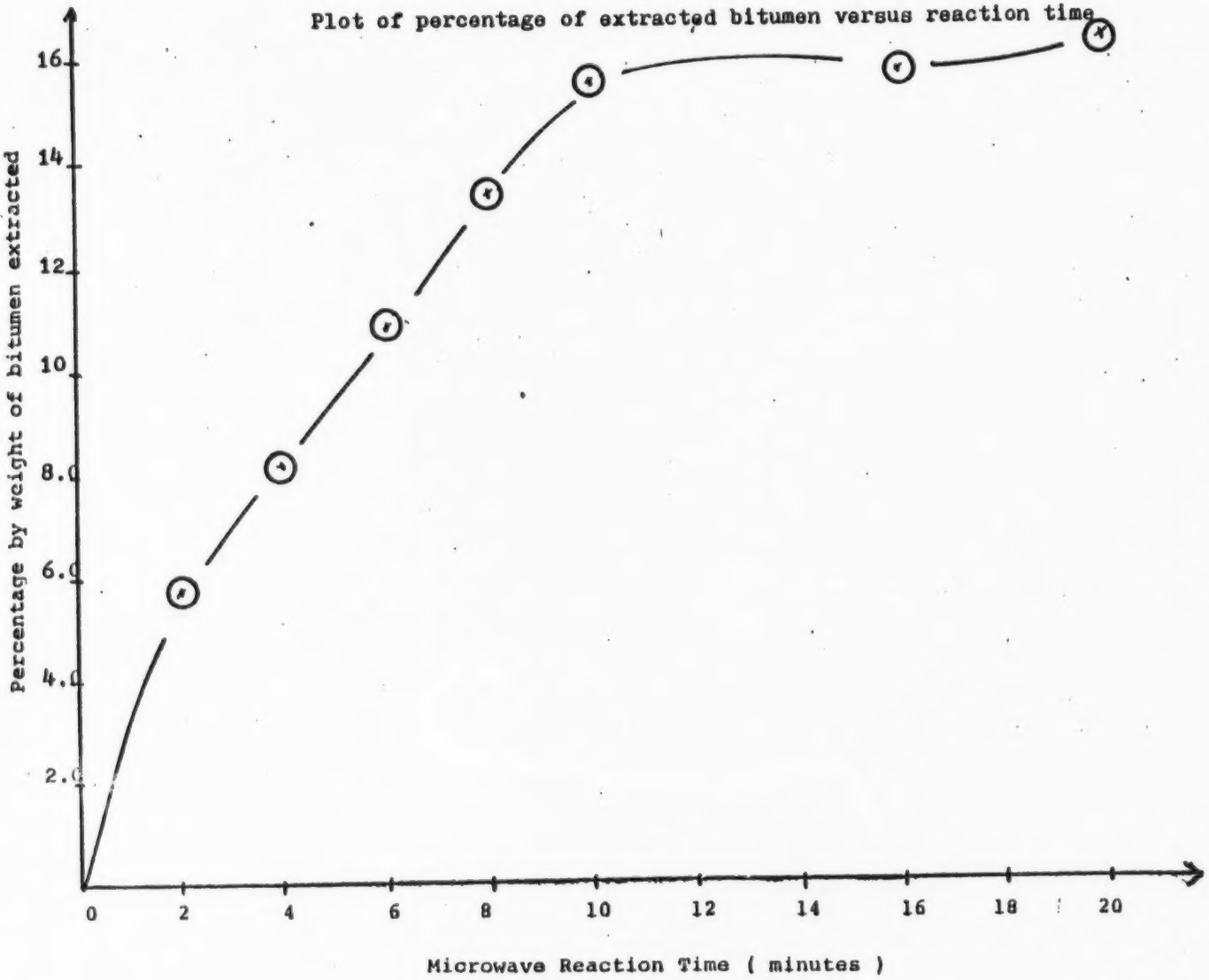
Sample A2-11

Plot of percentage of bitumen extracted versus reaction time



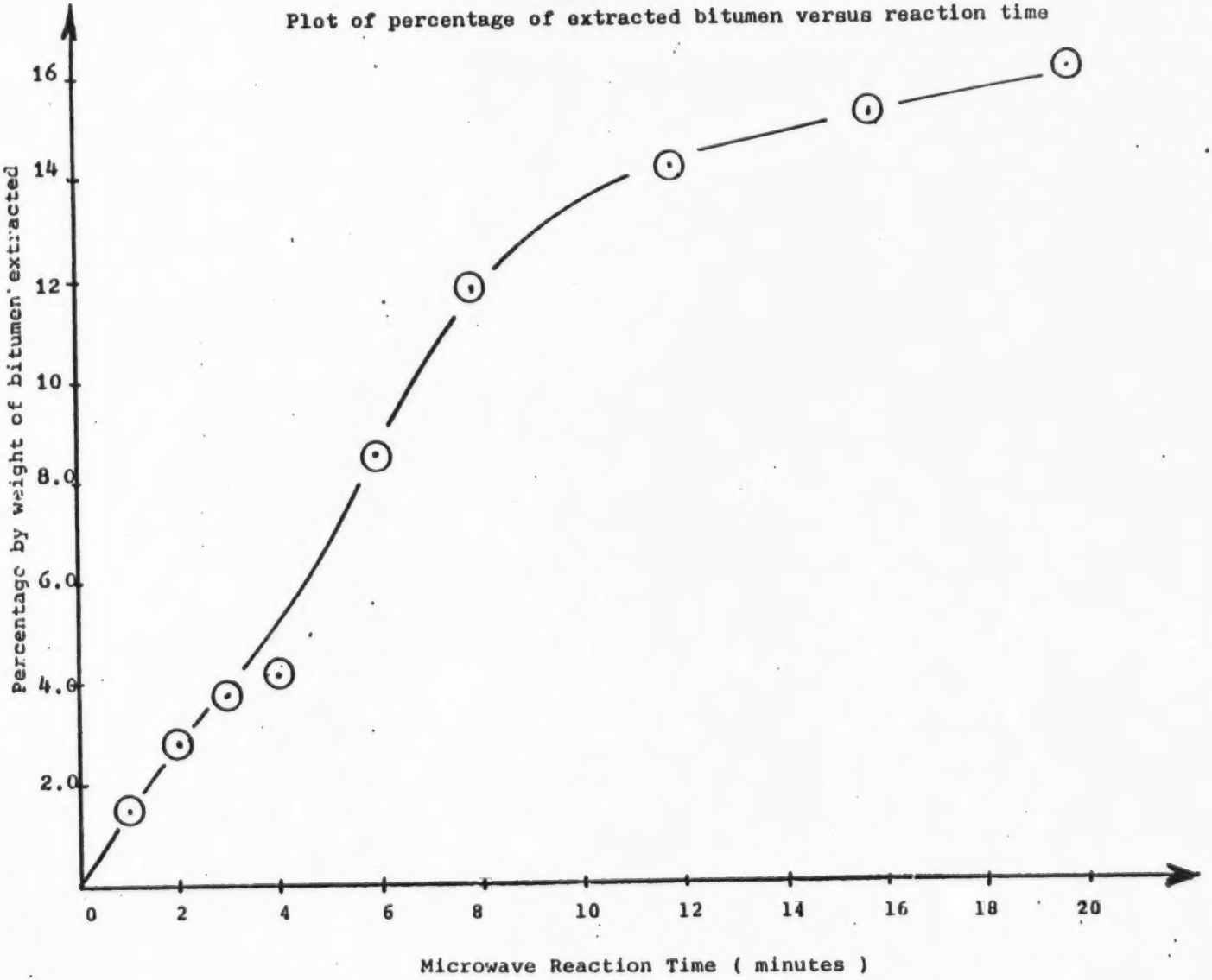
Sample A3-17

Plot of percentage of extracted bitumen versus reaction time



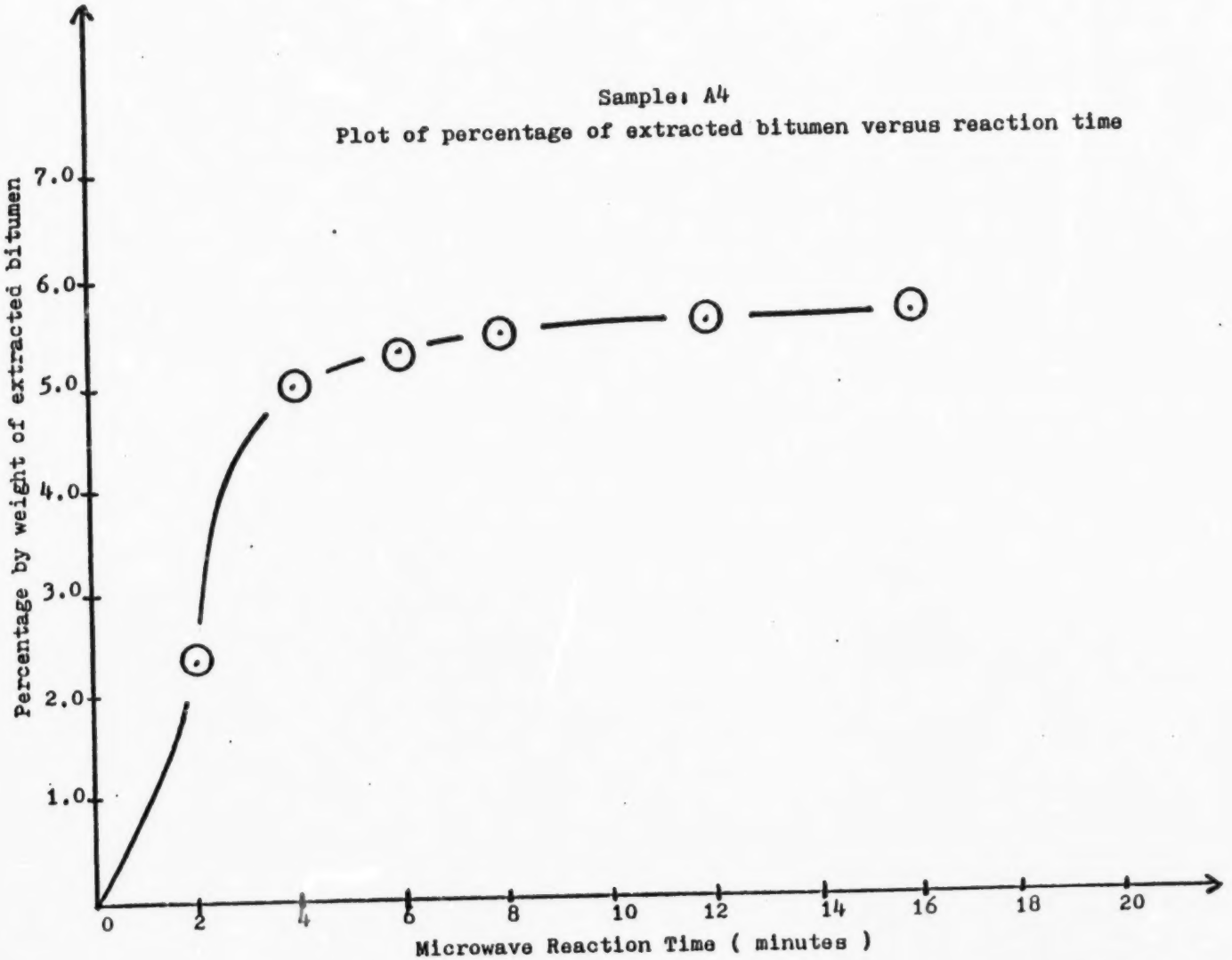
Sample: A3-04

Plot of percentage of extracted bitumen versus reaction time



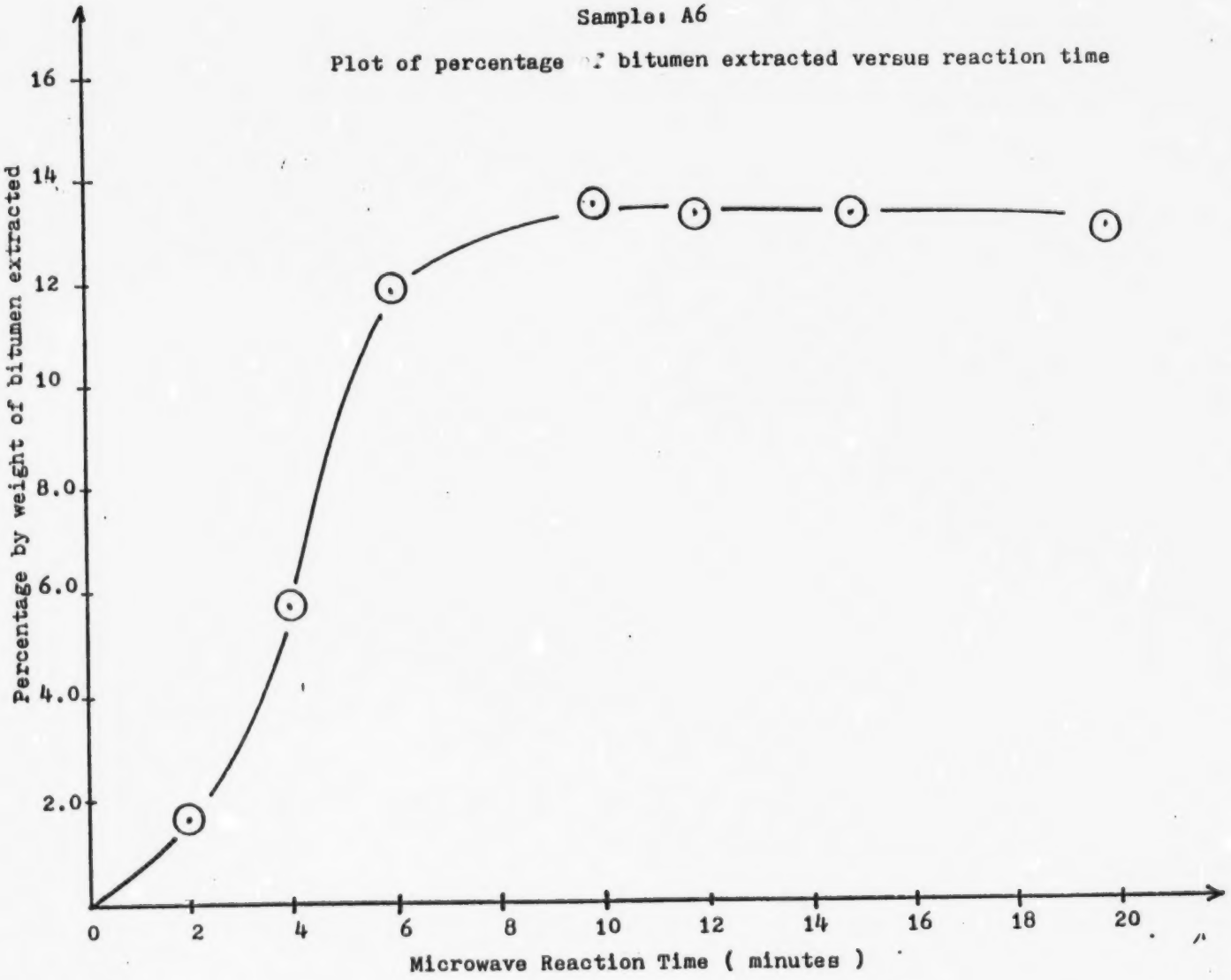
Sample: A4

Plot of percentage of extracted bitumen versus reaction time



Sample: A6

Plot of percentage of bitumen extracted versus reaction time

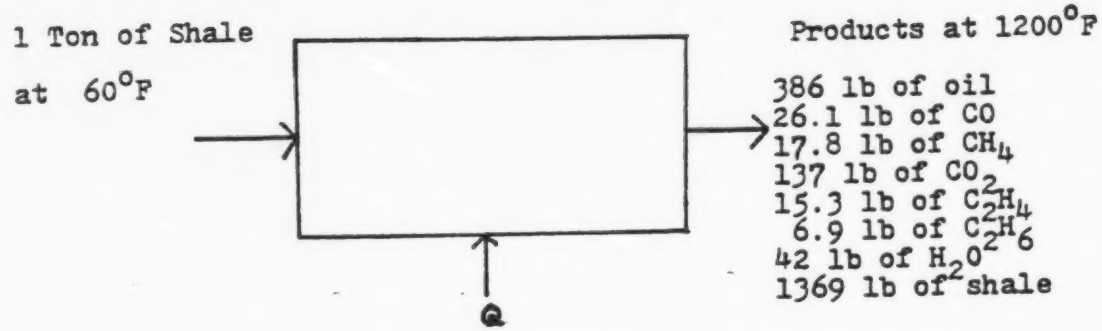


APPENDIX A4

SAMPLE CALCULATION

Theoretical Amount of Energy Required to Recover Oil

Based on Sample A1-07



Assumed Specific Heat Valves

Shale = 0.15 BTU/lb°F

Oil = 0.8 BTU/lb°F

Gas = 0.35 BTU/°F

Sensible Enthalpy of incoming Shale

$$H_{s_h} = 0.15 \left(2000 \frac{lb}{Ton}\right) (60-32) = 8400 \text{ BTU}$$

Energy Required to produce output conditions:

Oil: $H_{oil} = (.80)\ (386)\ (1200-32) = 360{,}680$ BTU

Gas: $H_{gas} = (.35)\ (203)\ (1200-32) = 82{,}990$ BTU

Spent Shale: $H_{ssh} = (0.15)\ (1369)\ (1200-32) = 239{,}850$ BTU

To Evaporate H_2O $H_2 = (42)\ (970 \text{ BTU/lb}) = 40{,}740$ BTU

Heat of Pyrolysis

Assume, for every g-mole of light hydrocarbon gas produced 15 kcal of energy are required.

G-moles of hydrocarbons

CH_4: $26.1 \text{ lb} \times \frac{454 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ g-mole}}{16 \text{ g}} = 740.5 \text{ g-mole}$

C_2H_4: $15.3 \times 454 \times \frac{1}{28} = 248 \text{ g-mole}$

C_2H_6: $6.9 \times 454 \times \frac{1}{30} = 104 \text{ g-mole}$

Total = 1092.5 g-mole

$$\text{Energy Required} = 1092.5 \text{ g-mol} \times 15{,}000 \frac{\text{cal}}{\text{g-mole}} = 16{,}387{,}500 \text{ cal.}$$

$$\text{Convert to BTU} = 16{,}387{,}500 \text{ cal} \times \frac{1 \text{ BTU}}{252 \text{ cal.}} = 65{,}030 \text{ BTU}$$

Mircowave Energy that must be supplied is therefore

ME = (65,030 + 239,850 + 40,740 + 82,990 + 360,680) - 8400

= 789,290 - 8400

= 780,890 BTU

Heating Value of Oil and Gases Produced

$$\text{Oil} = 386 \text{ lb} \times 18{,}000 \frac{\text{BTU}}{\text{lb}} = 6{,}948{,}000 \text{ BTU}$$

Gases based on Heats of Combustion at 25°C

$$CO: \quad 67{,}636 \frac{cal}{g\text{-mole}} \times 26.1\ lb \times \frac{454\ g}{1\ lb} \times \frac{1\ g\text{-mol}}{28\ g} \times \frac{1\ BTU}{252\ cal} = 113{,}600\ BTU$$

$$CH_4: \quad \frac{212{,}800 \times 17.8 \times 454}{16 \times 252} = 426{,}000\ BTU$$

$$C_2H_4: \quad \frac{337{,}234 \times 15.3 \times 454}{28 \times 252} = 332{,}000\ BTU$$

$$C_2H_6: \quad \frac{372{,}820 \times 6.9 \times 454}{30 \times 252} = 154{,}500\ BTU$$

TOTAL = 1,026,600 BTU

Total Heating Value of Products = 1,026,600+6,948,000

= 7,974,600 BTU

Ratio of Energy used to Energy Recovered $= \frac{780{,}890}{7{,}974{,}600}$

= 0.098

SAMPLE CALCULATION

Amount of Energy Required to recover oil based on Sample A1-07

Power Level = 100 Watts

Reaction Time = 15 minutes

Energy Required = Power Level x Reaction Time

$$= \frac{100 J}{s} \times 15\ Min. \times 60 \frac{sec.}{min.} \times \frac{1\ BTU}{1054.3\ J}$$

= 85.36 BTU

The Heating Value of Oil and Gas Recovered

Heating value of oil = 18,000 BTU/lb

Amount of Oil Recovered = 0.4042 g.

Energy Recovered = Amount x Heating Value

$$= 0.4042 \text{ g} \times \frac{1 \text{ lb}}{454 \text{ g}} \times 18{,}000 \frac{\text{BTU}}{\text{lb}}$$

$$= \underline{16.02} \text{ BTU}$$

Heat of Combustion of Gases Recovered (25°C)

Gas	Amount (g)	ΔH_c $\frac{(\text{Kcal})}{\text{g-mole}}$
CO	.02736	-67.636
CH_4	.01854	-212,800
C_2H_4	.01604	-337.234
C_2H_6	.00727	-372.820

Heating Value = $-\Delta H_c$ x Amount

CO: Heating Value = $67{,}636 \frac{\text{cal}}{\text{g-mol}} \times .02736\text{g} \times \frac{1\text{g-mol}}{28\text{g}} \times \frac{1 \text{ BTU}}{252 \text{ cal}}$

$= 0.262$ BTU

CH_4: Heating Value = $\frac{212{,}800 \times .01854}{16 \times 252} = \underline{.9785}$ BTU

C_2H_4: Heating Value = $\frac{337{,}234 \times 0.01604}{28 \times 252} = \underline{0.767}$ BTU

C_2H_6: Heating Value = $\frac{372{,}820 \times 0.00727}{30 \times 252} = \underline{0.3585}$ BTU

Total Heating Value of Gas = $\underline{2.37}$ BTU

Total Heating Value of Products = 16.02 2.37

= 18.39 BTU

Ratio of Energy Used to Energy Recovered = $\frac{85.36}{18.39}$

= 4.64